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Characterization of Oil Sands Fluid Coke

by

Simon Hung-kin Har



A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF Master of Science

IN

Metallurgical Engineering

Department of Mineral Engineering

EDMONTON, ALBERTA

Fall 1981



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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled Characterization of Oil Sands Fluid Coke submitted by Simon Hung-kin Har in partial fulfilment of the requirements for the degree of Master of Science in Metallurgical Engineering.

DEDICATION

To Caroline,
and to Aileen and Bryan

ABSTRACT

Syncrude fluid coke consists of black, fine and spherical particles with a size distribution similar to a fine beach sand. Its physical and chemical properties were determined as a function of particle size.

Syncrude fluid coke has a low atomic hydrogen to carbon ratio (0.25) and high sulphur content (7 wt %). Its ash content was about 7-8 wt %. It was found that smaller particles have a higher hydrogen content than that of larger particles.

The physical structure of Syncrude fluid coke was investigated by scanning electron microscopy. It was found that the coke is non-porous and has an 'onion skin' structure.

In multi-elemental analyses of the coke ash, it was found that most of the metals are associated with the mineral matter, except nickel and vanadium.

The Infrared spectra of the coke showed that the coke is very aromatic and the organic sulphur is likely in hetero-aromatic forms.

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1. Introduction

The first commercial fluid coker in the world was installed by Carter Oil Company at Billings, Montana, U.S.A. in 1954. The licenser of the process was Esso Research and Engineering Company [1]. Since then, about thirteen similar fluid cokers have been installed in the world [2]. Syncrude's fluid coker at Fort McMurray, Alberta, Canada is the latest and largest fluid cokers in the world [3].

The fluid coking process was developed by Esso Research Laboratories at Linden, New Jersey and Baton Rouge, Louisiana in the early 1950's. It was originally designed for upgrading crude residua and similar low grade oils. It aimed at competing with other residuum upgrading processes, such as the delayed coking process and the visbreaking process [4].

Syncrude Canada Limited, a consortium of several oil companies and governments, adopted the fluid coking process for upgrading bitumen extracted from Athabasca oil sands to synthetic crude oil. Syncrude's Mildred Lake tar sand complex was officially started up in late 1978. There are two fluid cokers installed at this complex. Each fluid coker can produce over 50,000 bbl. of synthetic crude oil per day [5].

The fluid coking process produces petroleum fluid coke as a solid by-product. The production rate of Syncrude fluid coke is about 95,570 kg per hour (733,000 tonnes per year)

[6]. At this stage, there is no particular commercial use for Syncrude fluid coke. It is now being stockpiled for future development [6].

Some publications on the properties of fluid coke exist, but not specifically on Syncrude fluid coke. Fluid coke consists of very hard, fine, non-porous particles [7,8]. The average particle size of fluid coke is about 100 mesh (150 microns) [1,6]. The ultimate yield of fluid coke from a fluid coking process is proportional to the Conradson carbon¹ of the feed stock [7].

The objective of this research is to characterize the nature of Syncrude fluid coke, in order to assist in the assessment of its potential. A knowledge of the properties of Syncrude fluid coke facilitates the prediction and explanation of its kinetics and mechanisms of gasification and combustion [1] . It also makes it possible to evaluate the economic feasibility of extracting some metals from the coke ash, especially nickel and vanadium.

¹ Conradson carbon is the wt % carbonaceous residue formed after evaporation and pyrolysis of a petroleum product.

2. Literature Review

It is necessary to understand the properties and chemical composition of Syncrude fluid coke feed stock, Athabasca bitumen, before investigating the nature of Syncrude fluid coke. The chemical composition of Athabasca bitumen was not known exactly until mid 1970's, because of the complex nature of bitumen.

2.1 Quality of Athabasca Bitumen

In 1975, Berkowitz and Speight [1] summarized data for Athabasca bitumen from several different sources . This summary is reported in Table 1. Through a private communication with Syncrude Canada Limited, it was found that the bitumen processed by the Syncrude fluid coking process was similar. Its properties are listed in Table 2. [16]

2.2 Chemical Composition of Athabasca Bitumen

The study of Athabasca bitumen composition was initiated by Boyd and Montgomery [2] in the early 1960's. They separated the bitumen into asphaltenes, resin and oil. Then, they performed structural analysis on some selected fractions [3,4]. The material was also investigated by Jones

Table 1. Some Properties of Athabasca Oil-sand Bitumens

Elemental Composition

Carbon	83.3±0.3 %
Hydrogen	10.3±0.1 %
Oxygen	1.1±0.3 %
Nitrogen	0.4±0.1 %
Sulphur	4.9±0.4 %

Molecular Weight

540 - 800

Hydrocarbon Types

Asphaltenes	18 - 25 %
Resins	29 - 35 %
Oils	45 - 49 %

Specific Gravity

1.02 (=6 - 9° API)

Conradson Carbon

14.3 %

Table 2. Properties of Syncrude Bitumen

Gravity	8.3° API
Conradson Carbon	12.9 %
Sulphur	4.9 %
Nitrogen	0.45 %
Nickel	80 ppm
Vanadium	250 ppm

and Moote [5], Nagy and Gagnon [6], and Bowman [7], during the 1960's.

Strausz et. al., in 1977, gave the most complete report on the composition of Athabasca bitumen [8]. They showed that Athabasca bitumen contains 17% asphaltenes and 83% deasphalted oil. The whole bitumen has an atomic hydrogen to carbon ratio (H/C) of 1.48, which is relatively low compared to typical crude oil processed at the refinery, which has an H/C of 1.80. About 50 wt % of bitumen is aromatic compounds. The majority of these aromatic compounds contain more than one aromatic ring.

2.3 Fluid Coking Process

The successful development of a fluid coking process by the Esso Research Laboratories was announced in 1953 at the 33rd Annual Meeting of the American Petroleum Institute by Voorhies and Martin [9,10]. The objective of developing the fluid coking process was to compete with other residuum upgrading processes, such as the delayed coking and the visbreaking processes [11].

The fluid coking process employs fluidized-solid technology. It does not use any external catalyst for thermal cracking of its feedstock, residuum or similar low grade oil. It depends on a circulating stream of finely divided coke particles to furnish both heat and a large

surface area for the coking reaction.

Since the fluid coke particles are continually formed and grow gradually in size during the coking process, particles are constantly withdrawn from the system. They are then sized, and the finer fraction is returned to the process to maintain a constant particle size coke inventory in the coker. The coarser fraction is considered to be a non-beneficial solid by-product of the fluid coking process and is stockpiled.

Although the first commercial fluid coker was installed in 1954, very little research work has been done on fluid coke. Voorhies and Martin [9,10] presented a discourse on the properties of the fluid coke produced from a pilot plant at the 33rd Annual Meeting of the American Petroleum Institute in 1953. There were three different feed stocks tested at the pilot plant. In 1954, Martin, Barr and Krebs gave essentially the same report in the Oil and Gas Journal [12]. The qualities of the feed stocks tested at the pilot plant are given in Table 3. Some properties of fluid coke produced from these feed stocks are listed in Table 4.

At the same pilot plant, Johnson and Wood [13] reported the results of ten different feed stocks analyses covering a range of feed quality. They found that the ultimate coke yield from the fluid coking process varied directly with the Conradson carbon of the feed stock.

Table 3. Quality of Feed Stocks for Fluid Coking Process

Crudes Source of Feed	South Louisiana		
	Mixture	Hawkins	Elk Basin
Elemental Composition (wt %)			
Carbon	87.3	85.1	86.4
Hydrogen	11.5	10.1	9.8
Sulphur	0.9	4.3	3.8
H/C Atomic Ratio	1.57	1.41	1.35
Gravity, ° API			
	13.2	4.2	2.0
Conradson			
Carbon (wt %)	14.0	24.5	30.0
Ultimate Yield of Coke From the Process (wt %)			
	16.0	27.5	34.0

Table 4. Some Properties of Fluid Cokes

Feed-stock Source	South Louisiana		
	Mixture	Hawkins	Elk Basin
	wt %		
Carbon	92.5	88.3	88.6
Hydrogen	1.6	1.9	1.8
Sulphur	1.4	7.0	1.3
Volatile Matter (1100° F)	0.6	0.9	1.3
Ash	0.785	0.332	0.370
Nickel	0.021	0.010	0.011
Vanadium	0.003	0.015	0.035
Iron	0.055	0.007	0.003

In 1979, Jack, Sullivan and Zajic [14] investigated the possibility of extracting some metals from the Athabasca oil sands cokes. One of the coke samples used was the fluid coke produced from the fluid coking of Athabasca bitumen at the Exxon Refinery at Baton Rouge, Louisiana. They reported that the fluid coke particles were non-porous and spherical and had a relatively smooth surface. Some properties of this fluid coke are given in Table 5.

Ambrose and Flynn [15] gave the estimated properties of Syncrude fluid coke (Table 6) at the 27th Canadian Chemical Engineering Conference, Calgary, Alberta, 1977. At the conference, they assessed the potential for utilizing Syncrude fluid coke.

In 1979, it was found that the actual ash content of Syncrude fluid coke was 7.08 % to 8.23 %, which was higher than the estimated value, 5.9 % [16].

2.4 Inorganic Matter in Fluid Coke

The only information available on inorganic matter in Syncrude fluid coke was revealed in a private communication from Syncrude Canada Limited [17]. The ash composition of Syncrude fluid coke is given in Table 7. This analysis was done by inductively coupled plasma emission spectroscopy.

Table 5. Some Properties of Athabasca Fluid Coke from Exxon Refinery at Baton Rouge, Louisiana

<u>Composition</u>	<u>(wt %)</u>
Carbon	81.55
Hydrogen	1.45
Nitrogen	1.62
Sulphur	3.30
Ash(12 hr., 500° C)	7.1
Nickel	0.066
Vanadium	0.159
Iron	0.257

Table 6. Estimated Properties of Syncrude Fluid Coke

<u>Composition:</u>	<u>(wt %)</u>
Carbon	81.3
Hydrogen	1.9
Nitrogen	1.7
Oxygen	0.5
Sulphur	8.7
Ash	5.9
Nickel	810 ppm
Vanadium	2560 ppm
 <u>Properties:</u>	
Hardgrove Index	15 - 12
Surface Area	10 m ² /g
Bulk Density	0.88 - 1.04 g/cc
Volatility	less than 2 %
 <u>Particle Size:</u>	
Micron	Culmulative wt% less than
100	0 - 19
200	36 - 62
400	78 - 94
1000	86 - 98
 <u>Ultimate Yield of Coke</u>	
<u>from the Process:</u>	9 - 10%

Table 7. Multi-elemental Analysis of Syncrude Fluid Coke

<u>Metals</u>	<u>% of Ash</u>
Al	13.12
Ba	0.12
Ca	3.24
Cd	0.11
Co	0.01
Cr	0.06
Cu	<0.01
Fe	5.69
K	1.87
Mg	0.85
Mn	0.18
Mo	0.11
Na	0.91
Ni	0.72
P	0.13
Pb	0.08
Sn	<0.01
Si	21.35
Ti	1.39
V	1.89
Zn	0.06
Zr	0.08

Since bitumen contains some petroleum porphyrins, which are capable of forming complexes with nickel and vanadium, it is possible that nickel and vanadium in fluid coke are mainly associated with organic matter rather than mineral matter. Champlin and Dunning [18] reported that in Athabasca bitumen, only one-tenth of the total petroleum porphyrins present is required to complex all of the vanadium and nickel present. Comparison with some typical crudes showed that Athabasca bitumen was unique in this respect.

3. Samples for Research

3.1 Source of Samples

Six batches of Syncrude fluid coke were obtained from Syncrude Canada Limited between 1978 and 1981 [1]. The date and the amount of each sample are listed in Table 8. All of the samples came without qualitative or quantitative analyses. The samples were taken directly from the fluid coking process in preference to the stockpile.

The appearance of all samples was the same. They consisted of black, fine and spherical particles. The coke particles were very dry. They were finely divided but not dusty, and no agglomeration was observed.

3.2 Sampling Method

Syncrude fluid coke consists of hard granular particles with a size distribution similar to a fine beach sand. Because of the apparent inhomogeneity of Syncrude fluid coke, the sampling technique plays an important role in determining the nature of Syncrude fluid coke.

The sampling method prescribed by the American Society for Testing and Materials (ASTM) Standard D 2013, was thought unsatisfactory for Syncrude fluid coke because reproducibility for chemical and physical tests was poor.

Table 8. Coke Samples used in Research

<u>Date</u>	<u>Amount (kg)</u>
Dec 7, '78	20
Sept 18, '79	20
May 29, '80	25
Aug 12, '80	80
Oct 28, '80	40
Jun 8, '81	80

In a preliminary study, some portions of Syncrude fluid coke samples were obtained by following the routine given by ASTM Standard D 2013. A No. 1 Tyler sample splitter (or riffler) was used to obtain representative portions of coke samples. The weight of each portion of sample used for proximate and ultimate analysis was about 2 to 3 grams. However, it was found that the reproducibility of the results was poor and unpredictable, especially for the ash content. Therefore, it was necessary to adopt another sampling method to overcome this difficulty.

The sampling method ultimately adopted in this research was based on particle size distribution. Coke samples were sieved before they were used for testing and analysis. Surprisingly, it was found that the reproducibility of the experimental results for each particle size range became very good. Ash content analyses became particularly consistent.

3.3 Particle Size Distribution

The testing sieves used for the particle size distribution study were Tyler standard screen scale sieves series. The mesh designation used throughout the research was Tyler's mesh designation [2]. The difference amongst different mesh designations such as American and Canadian designations can be found in the Appendix.

Additional equipment used for sieving included a Tyler Ro-Tap testing sieve shaker, which was built to accommodate eight inch diameter testing sieves [2]. Since Syncrude fluid coke consisted of very fine particles, about 200 grams of coke particles were sieved each time in order to prevent blinding of the sieves. This was repeated several times, until about 3.5 kg of samples were totally sieved. The different particle sizes were stored separately for subsequent physical and chemical analysis.

The particle size distributions for all six samples are listed in Tables 9 and 10. The results showed that there was no significant change in the pattern for particle size distribution (Figures 1 and 2), with the exception that coke samples were getting finer in the more recent samples. The distribution patterns revealed that the major particle size, by weight, was 100 mesh (Figure 3).

Table 9. Particle Size Distribution of Syncrude Fluid Coke,
Part 1.

	<u>wt %</u>		
<u>Mesh Size</u>	<u>Dec 7, '78</u>	<u>Sept 17, '79</u>	<u>May 29, '80</u>
-200	6.0	4.1	10.8
200	3.2	3.3	2.9
170	7.6	9.4	10.8
150	7.4	9.7	10.0
115	9.2	10.8	10.3
100	22.3	25.1	20.2
80	12.7	12.9	10.2
65	10.4	10.4	8.1
60	8.3	6.8	7.8
48	3.8	3.6	3.2
42	3.8	2.1	1.8
+42	5.3	1.8	4.8

Table 10. Particle Size Distribution of Syncrude Fluid Coke,
Part 2.

	<u>wt %</u>		
<u>Mesh Size</u>	<u>Aug 12, '80</u>	<u>Oct 28, '80</u>	<u>Jun 8, '81</u>
-200	12.9	8.3	5.1
200	6.3	6.2	4.3
170	11.1	9.8	7.7
150	8.5	11.6	22.8
115	10.7	18.3	22.0
100	20.4	15.7	14.2
80	8.2	8.4	8.7
65	7.0	8.1	7.3
60	6.7	4.1	2.3
48	2.3	1.6	1.4
42	1.4	1.0	0.9
+42	4.5	6.9	3.3

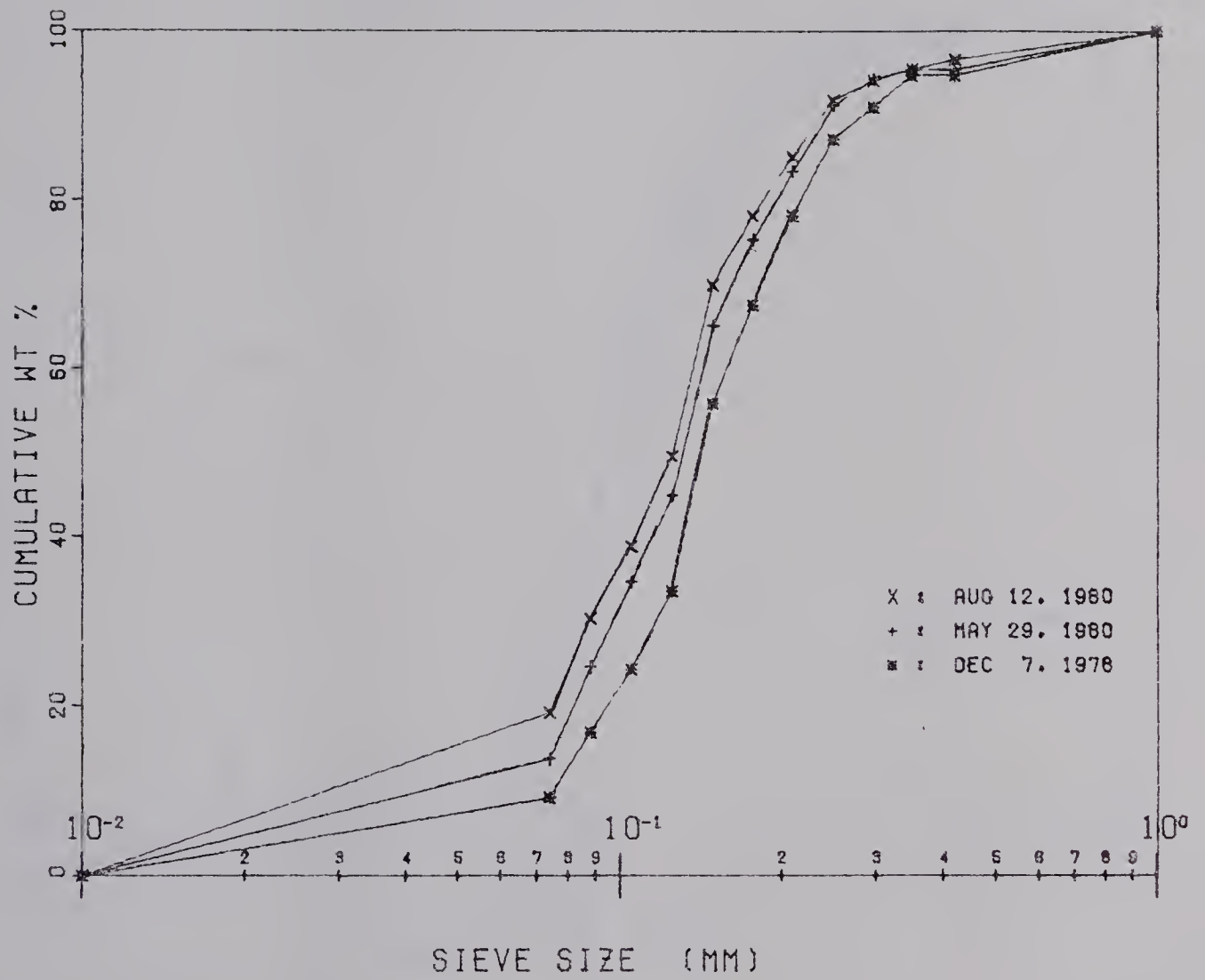


Figure 1. Particle Size Distribution for Syncrude Fluid Coke, Part 1.

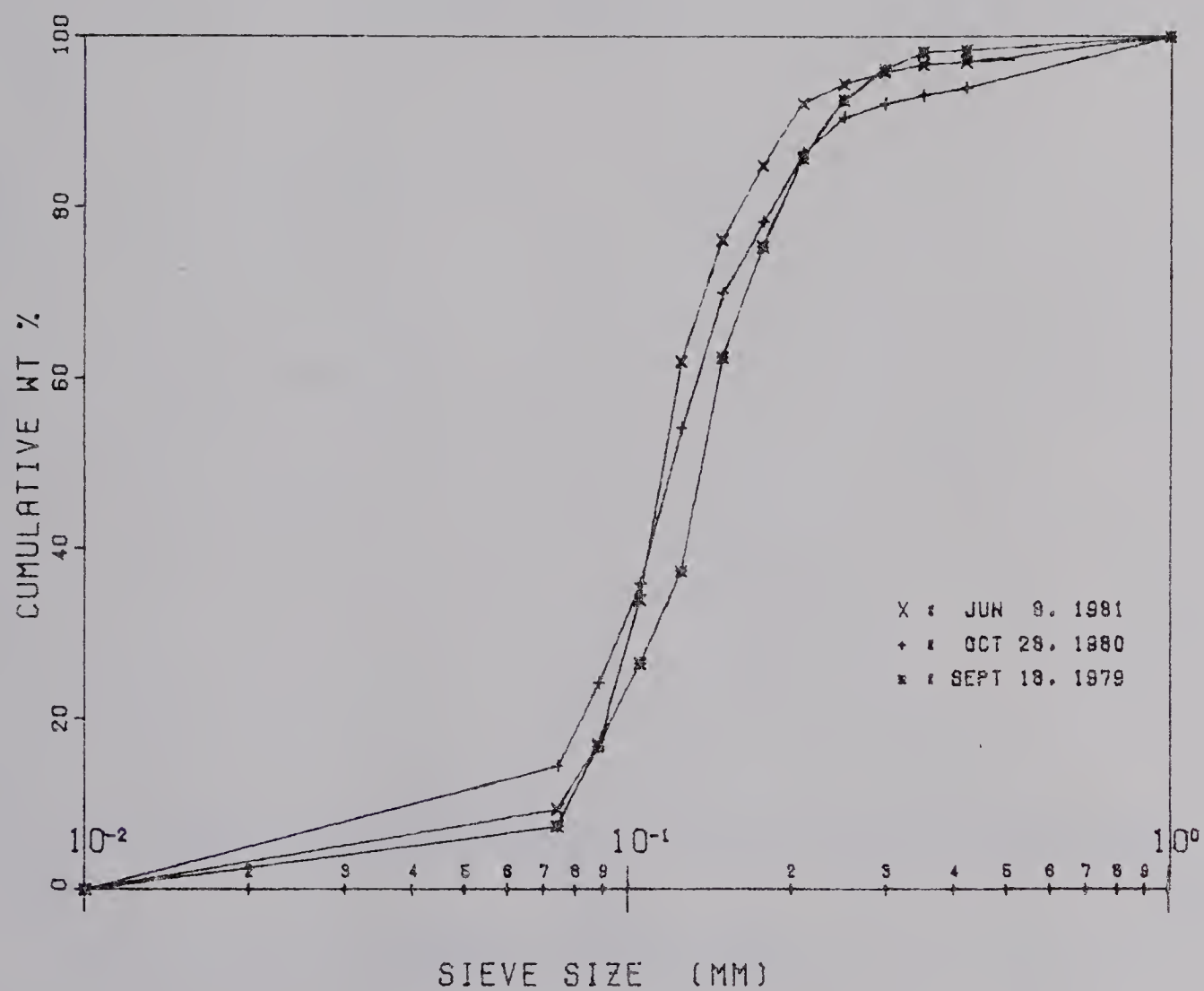


Figure 2. Particle Size Distribution for Syncrude Fluid Coke, Part 2.

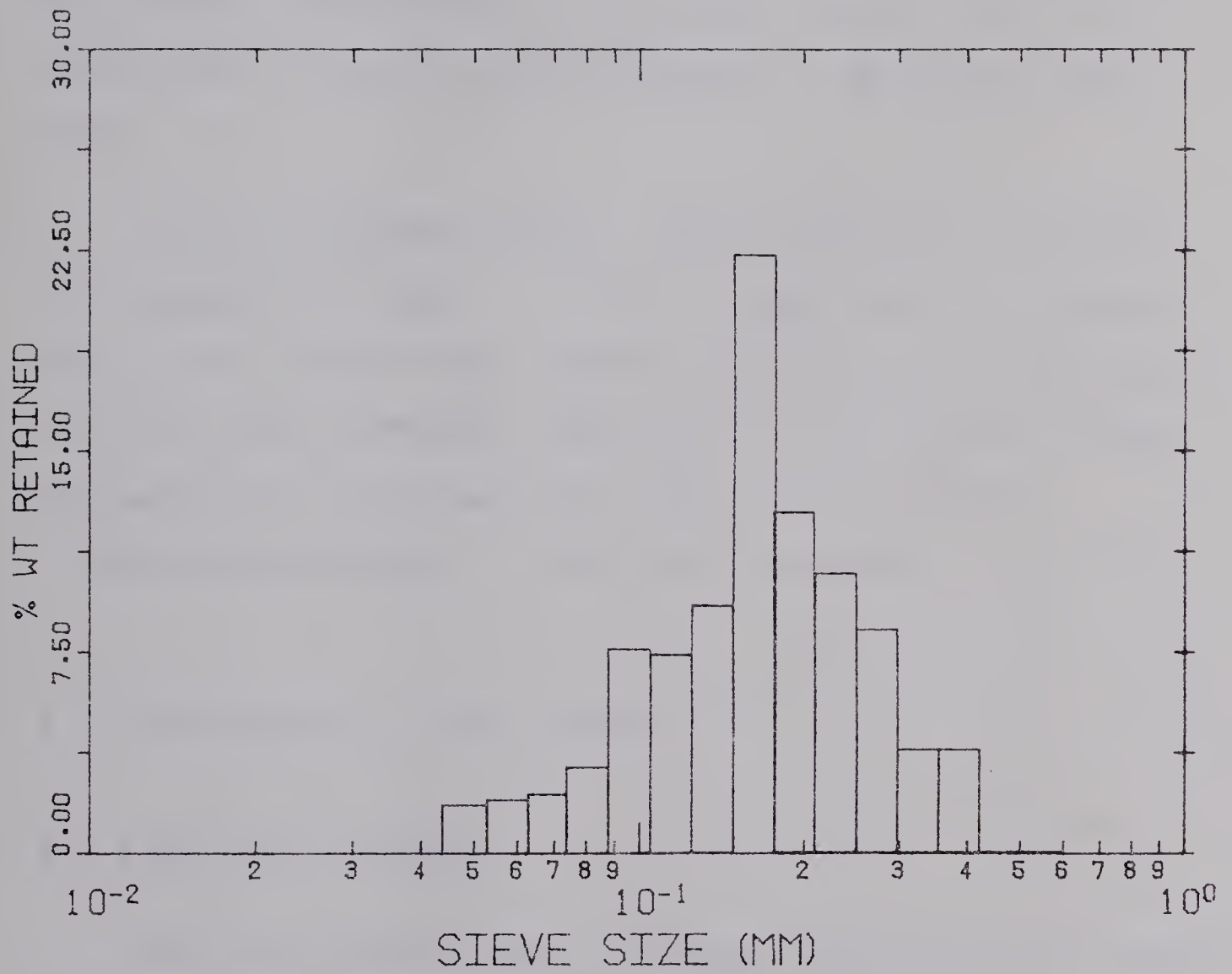


Figure 3. Histogram of Coke Size Distribution, Dec 7, '78.

4. Proximate Analysis

A typical proximate analysis of Syncrude fluid coke is listed in Table 11 [1]. The results in Table 11 are averaged over all particle sizes. From these results, it is seen that Syncrude fluid coke changes its characteristics from day to day. Hence, these results do not give a great deal of significant information on the nature of Syncrude fluid coke.

In the preliminary study, three portions of unsized coke samples from Dec 7, '78 were ashed. The ash contents were 7.3%, 7.5% and 7.8%. These results were too imprecise and hence not acceptable. Therefore, an ash content study was applied to every particle size range to better understand the nature of Syncrude fluid coke.

4.1 Determination of Ash Content

4.1.1 Methods of Ashing

There are two methods of ashing, low temperature ashing (L.T.A.) and high temperature ashing (H.T.A.).

Low temperature ashing, also known as electronic low temperature ashing or radio-frequency ashing, was originally developed by Gleit and Holland [2]. In this ashing method, oxygen is passed through a high energy electromagnetic field

Table 11. Typical Proximate Analysis of Syncrude Fluid Coke

<u>Date</u>	<u>Aug 7, '79</u>	<u>Aug 31, '79</u>
Ash (%)	8.23	7.08
Volatile Matter (%)	5.73	6.24
Moisture (%)	0.79	0.47
Fixed Carbon (%)	85.25	86.21
Bulk Density (g/cc)	1.04	1.09

generated by a radio-frequency oscillator. As the oxygen is passing through the radio-frequency field, a discharge takes place, and consequently a mixture of atomic and ionic species are formed. When the activated oxygen passes over an organic substance such as coal or coke, oxidation will take place at a relatively low temperature. This temperature is usually lower than 150° C.

The main advantage of L.T.A. is that the minerals present in coke are not affected to any appreciable degree. However, ashing a few grams of coke may take several days for completion. During this long ashing process, some organic sulphur may be fixed as sulphate, especially when a sample contains a large amount of calcium [3].

High temperature ashing involves ashing a coke sample in a muffle furnace at a temperature above 500° C. During high temperature ashing, some minerals change their states, (e.g. sulphides become oxides), and as a result of high temperature some volatile elements may be lost. The advantage of H.T.A. is that ashing may be completed in a few hours and that a muffle furnace can handle several samples at a time.

4.1.2 Experimental Procedure

In the preliminary study, the L.T.A. technique was used, but it was abandoned after a few trials because of the

prohibitive amount of time required to ash a few grams of coke. Hence, most of ashing was done by H.T.A.

The furnace used for H.T.A. was a Lindberg tube furnace, Model 54241. About 2.5 grams of a coke sample was weighed to the nearest 0.1 mg in a porcelain combustion boat, and ashed gradually from room temperature to a desired temperature in the tube furnace.

The time and temperature for ashing was investigated by a series of tests. Triplicates of 100 mesh coke samples of Dec 7, '78 were ashed at four different temperatures, until a constant weight of ash was obtained. Surprisingly, the consistency of the ash content of this particular particle size was very good. The relative deviation was less than 0.5 percent. The ashing results are listed in Table 12. From these results it was concluded that all the high temperature ashings would be conducted at $800 \pm 10^\circ \text{C}$ for seven hours.

4.1.3 Results and Discussion

The ash content of four different batches of coke, (Dec 7, '78, May 29, '80, Aug 12, '80 and Oct 28, '80), was determined for every particle size. Triplicates of each sample were ashed. The relative deviation of the ash content was less than 0.5 %, which is surprisingly good. The results are listed in Table 13 and plotted on Figure 4. From the results, it is evident that all batches of coke show a

Table 12. Time and Temperature Studies on Coke Ashing

<u>Temperature (°C)</u>	<u>Time (hours)</u>	<u>Ash (wt %)</u>
500	14	8.09
600	12	7.97
700	9	7.70
800	7	7.54

Table 13. Ash Content of Syncrude Fluid Coke

<u>Mesh</u>	<u>Dec 7, '78</u>	<u>wt %</u>		
		<u>May 29, '80</u>	<u>Aug 12, '80</u>	<u>Oct 28, '80</u>
200	8.21	8.35	8.39	8.20
170	8.20	8.27	8.39	8.19
150	8.10	8.05	8.31	8.18
115	7.84	7.94	8.34	7.88
100	7.53	7.68	8.27	7.73
80	7.28	7.61	8.19	7.71
65	7.06	7.58	8.20	7.86
60	6.97	7.56	8.16	8.37
48	6.95	7.68	8.17	8.67
42	7.08	8.14	8.25	8.84
35	7.94	8.32	8.49	9.05

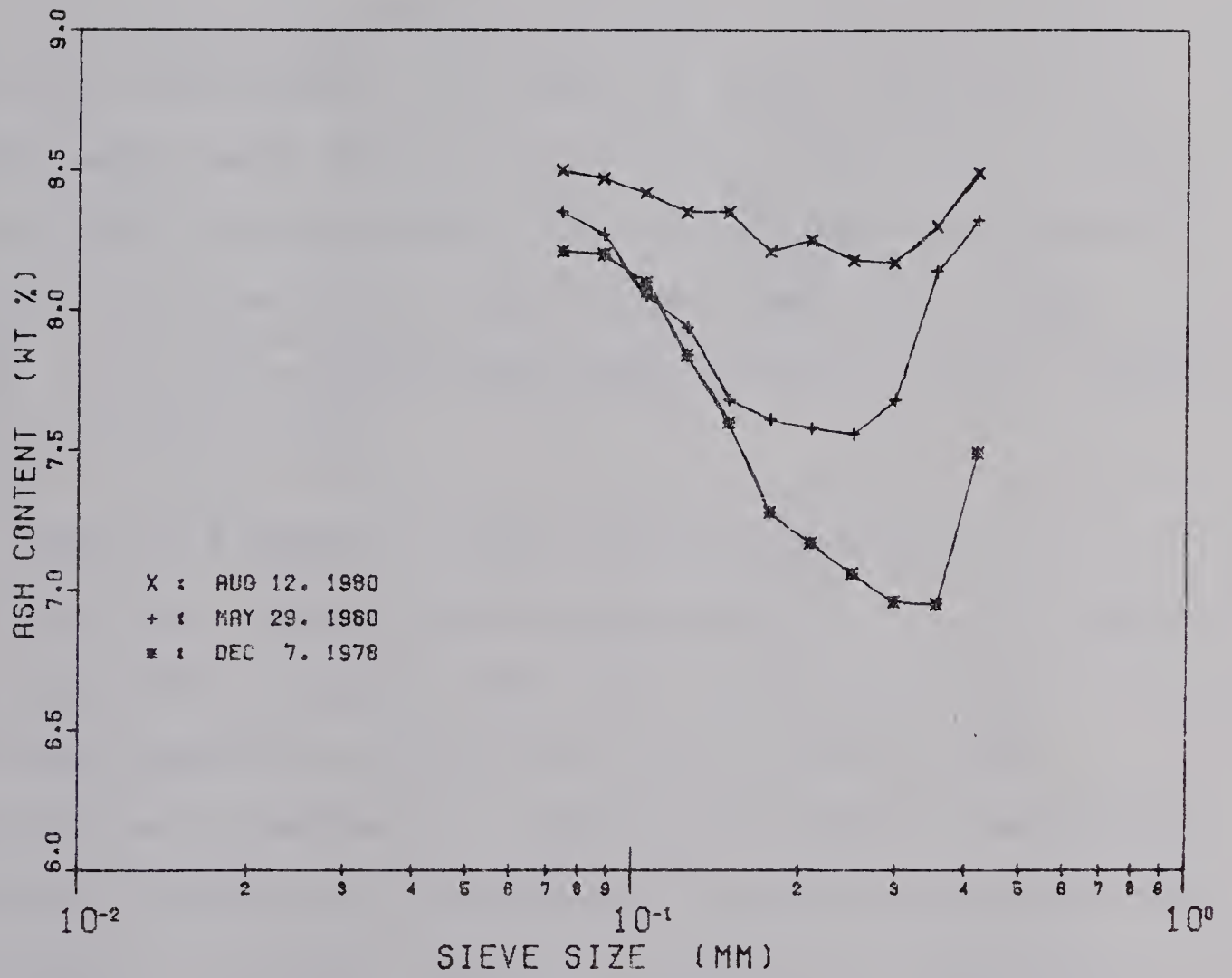


Figure 4. The Ash Content of Fluid Coke as a Function of Particle Size.

similar trend of ash content with respect to particle size. The results are calculated on an as received basis.

4.2 Determination of Moisture Content and Volatile Matter

4.2.1 Experimental Procedure

Both moisture and volatile matter of Syncrude fluid coke were determined in an apparatus which consisted of a custom-made quartz tube with stopcocks at both ends, a tube furnace and a vacuum system. The vacuum system consisted of a five-outlet manifold, a cold-finger trap and a vacuum pump. This vacuum system was capable of maintaining a vacuum of less than 0.05 torr.

About 2.5 grams of a coke sample were placed in a porcelain boat and weighed to the nearest 0.1 mg. This was then put into the quartz tube which could take three porcelain boats at a time. One of the outlets of the manifold was connected to a stopcock attached to the quartz tube and turned on for evacuation. The tube furnace was then switched on and heated slowly to the desired temperature. The coke samples were devolatilized for 24 hours.

4.2.2 Results and Discussion

The reproducibility of the volatile matter and moisture content determination was not as good as that of the ash content determination; the relative deviation was about 10 % even for the same particle size. This may have been caused by the limitation of the method and/or the inhomogeneity of the coke. However, some interesting data were found in the results (Table 14 and Figure 5). The results suggest that carbonization of Syncrude fluid coke takes place at about 700° C. Table 14 is a summary of the devolatilization of unsized coke samples of Dec 7, '78 at eight different temperatures. At temperatures greater than 800° C, some coke particles were ejected from the porcelain combustion boat because of rapid discharge of volatile material. Hence, no accurate results were obtained beyond this temperature.

Table 14. Coke Loss due to Destructive Distillation

<u>Temperature (° C)</u>	<u>Weight Loss (wt %)</u>
100	0.8
200	1.2
300	1.7
400	2.2
500	2.8
600	3.2
700	5.6
800	7.0

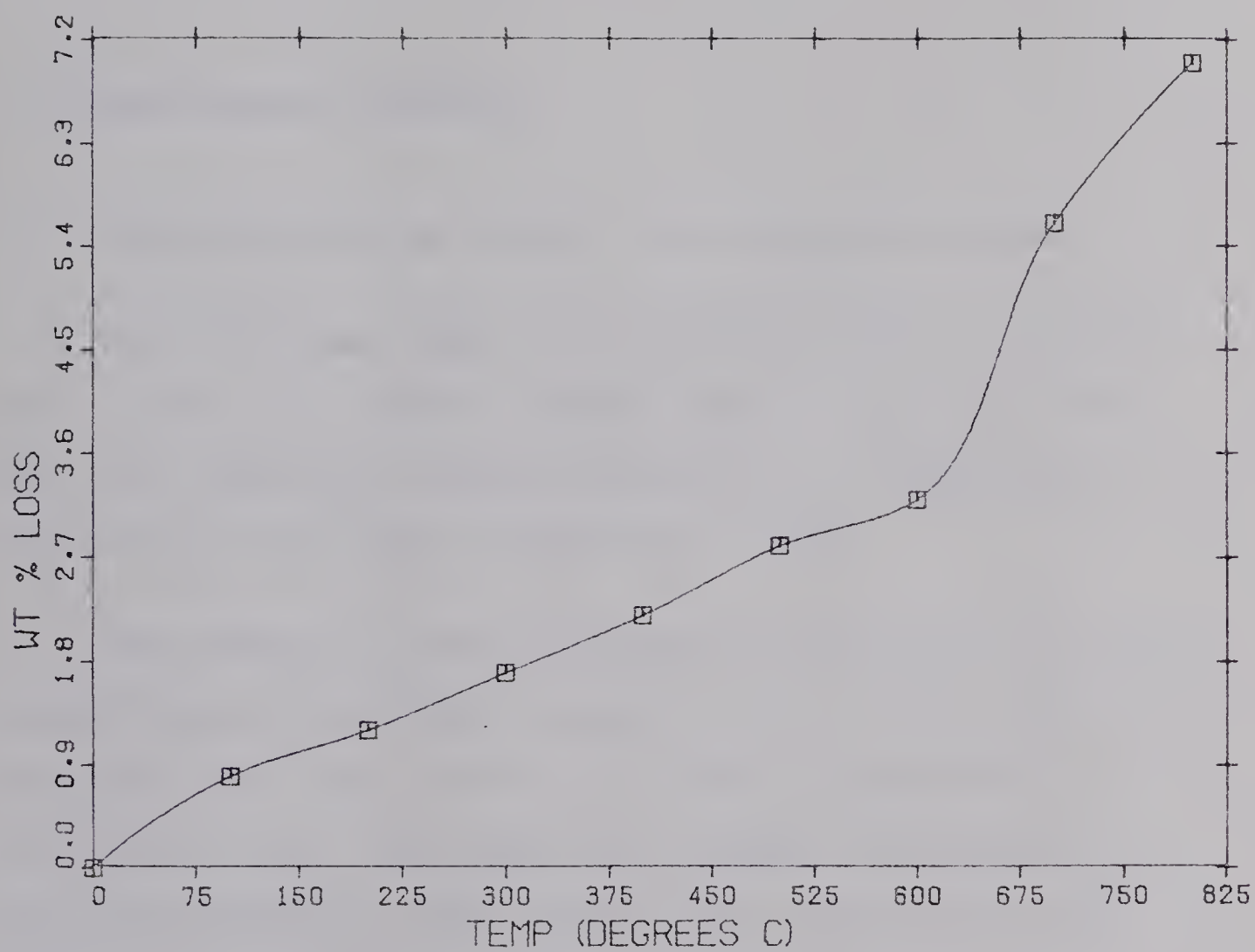


Figure 5. Wt % of Coke Loss as a Function of Temperature.

5. Ultimate Analysis

The ultimate analysis encompassed the quantitative determination of carbon, hydrogen, nitrogen, oxygen and organic sulphur which make up the organic matter of the coke. The analyses were done by conventional oxidation and/or reduction methods.

5.1 Experimental Procedure

5.1.1 Determination of Carbon, Hydrogen and Nitrogen

The instrument used for determining carbon, hydrogen and nitrogen was a Perkin-Elmer elemental analyzer Model 240B. The elemental analyzer consists of 2 components, a combustion train and an analytical system.

The combustion train included two independently heated combustion and reduction furnaces, each with the appropriate reaction tube. About 2-3 mg of a finely ground and previously dried coke sample was weighed and placed in a platinum combustion boat. It was then inserted into the combustion tube of the elemental analyzer where it was combusted in an excess of pure oxygen under static conditions. The combustion took place at about 950° C. The reduction tube, which was heated to 650°-700° C, reduced any nitrogen oxides to nitrogen gas and removed any residual oxygen from the combustion train.

The combustion products, carbon dioxide, water and nitrogen, were then mixed homogeneously with helium which served as the carrier gas. Three pairs of thermal conductivity cells arranged in series were used for detection in the analytical system, one pair each for water, carbon dioxide and nitrogen. The platinum filaments of each cell pair were connected differentially in a bridge circuit so that any difference in the contents of two cells would result in an electrical signal. A magnesium perchlorate trap between the first pair of cells absorbed any water from the gas mixture before it entered the second cell. Therefore the signal obtained from the corresponding bridge circuit was proportional to the amount of water removed. Likewise, an Ascarite (NaOH coated on asbestos) trap between the second pair of cells resulted in a signal in proportion to the carbon dioxide removed from the sample. The last pair of cells detected nitrogen by comparing the thermal conductivity of the remaining sample gas with that of pure helium.

5.1.2 Determination of Oxygen

The instrument used for determining oxygen in the coke sample was a modified Perkin-Elmer elemental analyzer Model 240B. Instead of combusting the sample in pure oxygen, 2-3 mg of the finely ground and previously dried coke sample was heated to over 1000° C in pure helium on the assumption that

all the organic oxygen would combine with carbon to form carbon dioxide. Hence, oxygen was determined as carbon dioxide by the thermal conductivity detector.

5.1.3 Determination of Sulphur

2-3 mg of a finely ground and previously dried coke sample was weighed, placed in a platinum sample holder and combusted quantitatively in a flask containing pure oxygen and 5 ml of diluted hydrogen peroxide. During combustion organic sulphur was oxidized to sulphur dioxide and dissolved in the hydrogen peroxide solution. The dissolved sulphur dioxide was then oxidized by hydrogen peroxide to sulphuric acid. The final solution was titrated gravimetrically with barium perchlorate solution using thorin as an end-point indicator.

5.2 Results and Discussion

The batch from Dec 7, '78 was selected for ultimate analysis. Duplicates of coke samples for each particle size were used for hydrogen, carbon, nitrogen and sulphur determinations. Only one sample of each particle size was used for oxygen determination. All the elemental analyses was reported on a dry basis.

The reproducibility of the hydrogen and carbon determinations was very good; the absolute deviations for

hydrogen and carbon were about $\pm 0.01\%$ and $\pm 0.1\%$, respectively (Table 15). However, the reproducibility of nitrogen and sulphur was poor as indicated in Table 16 and Table 17. This might be due to the random distribution of nitrogen and sulphur in bitumen (Figure 7).

From Table 15, it is observed that the smaller particles have a higher hydrogen content and lower carbon content. In other words, the hydrogen to carbon ratio (H/C) decreases as the particle size increases (Figure 6 and Table 15). This may be because the smaller particles have more surface area per unit volume for the adsorption of bitumen, or because the larger particles are more poly-aromatic in nature as a result of their longer residence times in the fluid coker for carbonization.

In these determinations it was assumed that interference from matter, such as mineral carbonates and sulphides, was minimal.

Table 15. Hydrogen and Carbon Contents of Syncrude Fluid Coke, Dec 7, '78.

<u>Mesh Size</u>	<u>Hydrogen</u>	<u>Carbon</u>	<u>H/C ratio</u>
170	1.67±0.01%	79.0±0.0%	0.253
150	1.65±0.02%	79.6±0.1%	0.249
80	1.61±0.01%	80.5±0.1%	0.240
60	1.51±0.01%	81.4±0.2%	0.223
48	1.50±0.01%	80.5±0.1%	0.224

Table 16. Oxygen and Nitrogen Contents of Syncrude Fluid Coke, Dec 7, '78.

<u>Mesh size</u>	<u>Nitrogen</u>	<u>Oxygen</u>
170	1.53±0.19%	2.54%
150	1.60±0.20%	2.48%
80	1.31±0.11%	2.51%
60	1.33±0.17%	2.49%
48	1.43±0.04%	2.33%

Table 17. Sulphur Content of Syncrude Fluid Coke, Dec 7, '78.

<u>Mesh Size</u>	<u>Sulphur (wt %)</u>
200	6.05±0.02
170	6.18±0.13
150	6.34±0.08
80	5.77±0.06
65	6.88±0.08
60	5.81±0.18
48	6.37±0.10
42	6.25±0.11
35	7.04±0.03

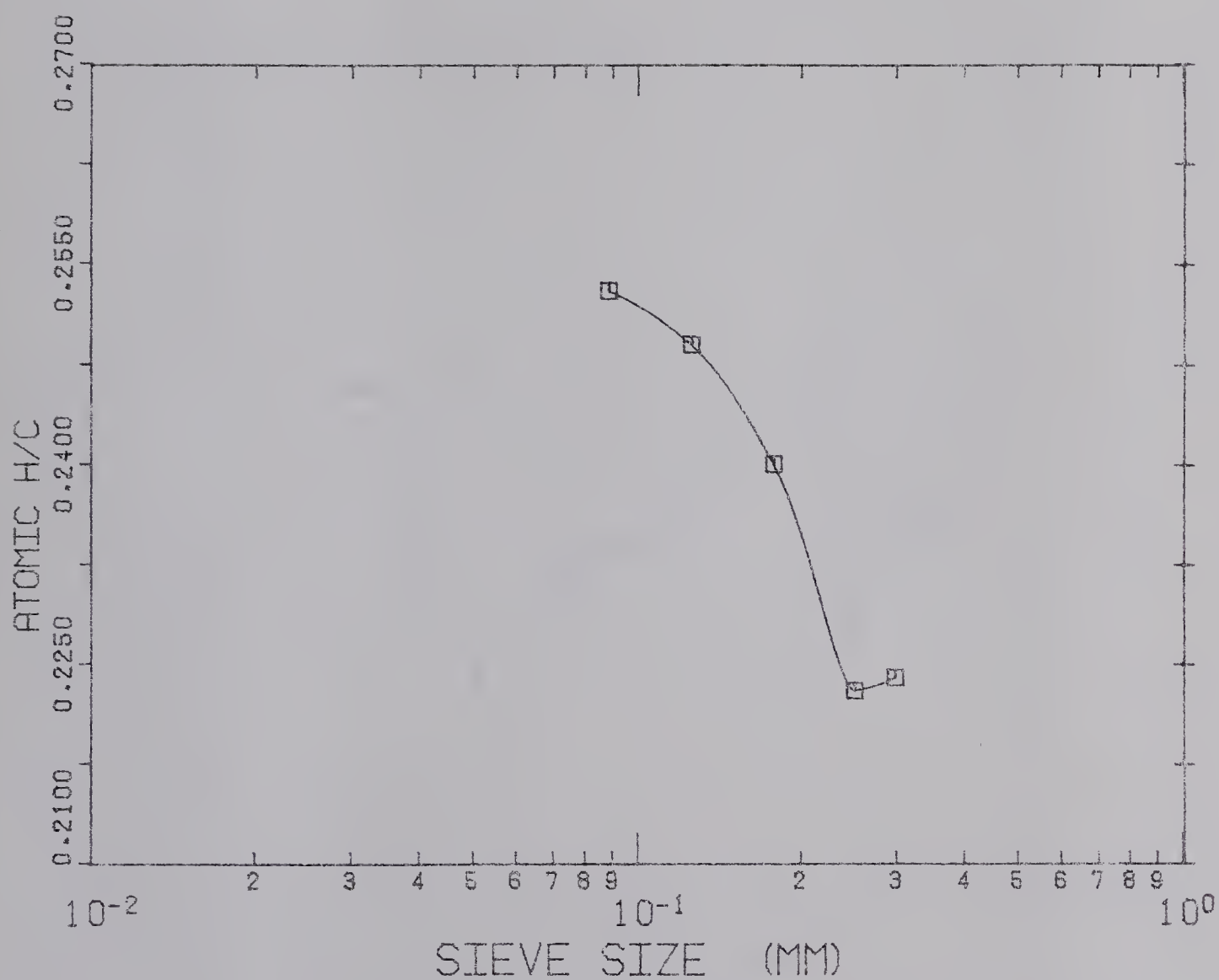


Figure 6. Hydrogen to Carbon Ratio as a Function of Particle Size, Dec 7, '78.

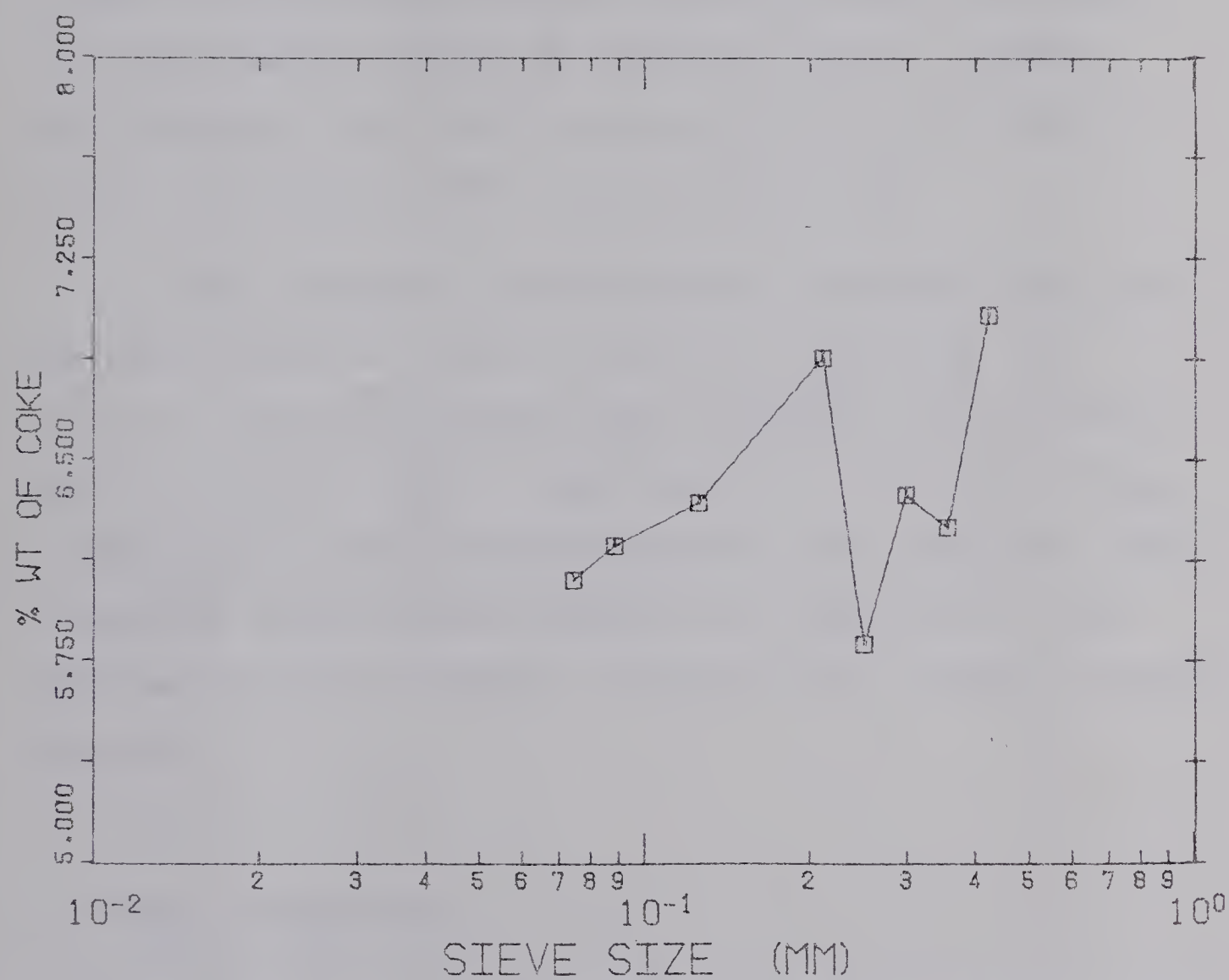


Figure 7. Sulphur Content as a Function of Particle Size,
Dec 7, '78.

6. Scanning Electron Microscopy

Jack, Sullivan and Zajic [1] used scanning electron microscopy to study the structure of three different kinds of petroleum cokes (fluid coke, flexicoker coke and delayed-coker coke), which were all produced from Athabasca bitumen. It was found that the fluid coke particles had a relatively smooth surface and were not porous. However, their work was very brief, as they were only interested in extracting minerals from the petroleum cokes.

In this research, the structure of Syncrude fluid coke was also studied by scanning electron microscopy. The scanning electron microscope used was Model ISI-60 made by International Scientific Instruments, Inc. This microscope is equipped with an energy dispersive x-ray analyzer, which is capable of performing nondestructive qualitative and semi-quantitative elemental analyses while a sample is being observed.

6.1 Sample Preparation

Both coke particles and coke ash particles were studied by scanning electron microscopy. The coke samples were dried in a vacuum furnace for 24 hours at 110° C to remove any moisture and volatile matter adsorbed on the coke surface. The coke ash particles were prepared by ashing some coke particles at 500° C for 12 hours. The coke particles were

ashed at a relatively low temperature to avoid the destruction of the coke particle skeletons. Also, some coke particles were partially oxidized in an electronic low temperature asher for 24 and 48 hours.

The samples were mounted on aluminum sample holders with high purity conductive silver paste. After mounting, the samples were coated with a layer of gold (about 200 Angstroms thick) . The coating instrument was an ISI - SPUTTERER-COATER Model P-S1. Sample coating was necessary because scanning electron microscopes work only with conductive materials. While the samples were investigated under the scanning electron microscope they were selectively photographed by a Polaroid camera. Also, some qualitative and semi-quantitative studies were done on selected regions of the sample particles using the energy dispersive x-ray analyzer.

6.2 Results and Discussion

The general appearance of the coke particles is shown in Figures 8 - 10. The particles are spherical and non-porous. The actual diameters of the particles can be measured directly from these electron photomicrographs. This confirms that the sieving of the coke particles was done properly. In Figure 11, a 100 mesh coke particle magnified 1000 times shows that it does not have any visible pores.

This can be explained by the fact that it was formed and grown by surface deposition of material.

A 42 mesh Coke particle was fractured mechanically. The internal structure of the fractured particle reveals an 'onion skin' or 'sedimentary rock' structure (Figures 12 - 16).

The ash particles retain the skeleton of the spherical structure of coke particles (Figure 17-19), but are more porous. The 'onion skin' structure is more prominent in ash particles (Figure 20) than in the coke (Figure 13). Part of the outer layer of the ash particle in Figure 20 is peeled off. Its appearance is like an 'ivory ball', in that it exhibits layers of concentric spherical shells. This confirms that the growth of a coke particle is by surface deposition of material.

The multi-layered structure of the fluid coke particles is best shown by electron photomicrographs of coke particles which had been partially oxidized using the low temperature ashing technique. Figure 21 and Figure 22 are electron photomicrographs of 60 mesh coke particles which had been partially oxidized in a low temperature asher for 24 and 48 hours, respectively. The organic matter of the outer layers has been oxidized leaving only the mineral matter behind. Since the low temperature ashing method is more static than the high temperature ashing method, the multi-layered

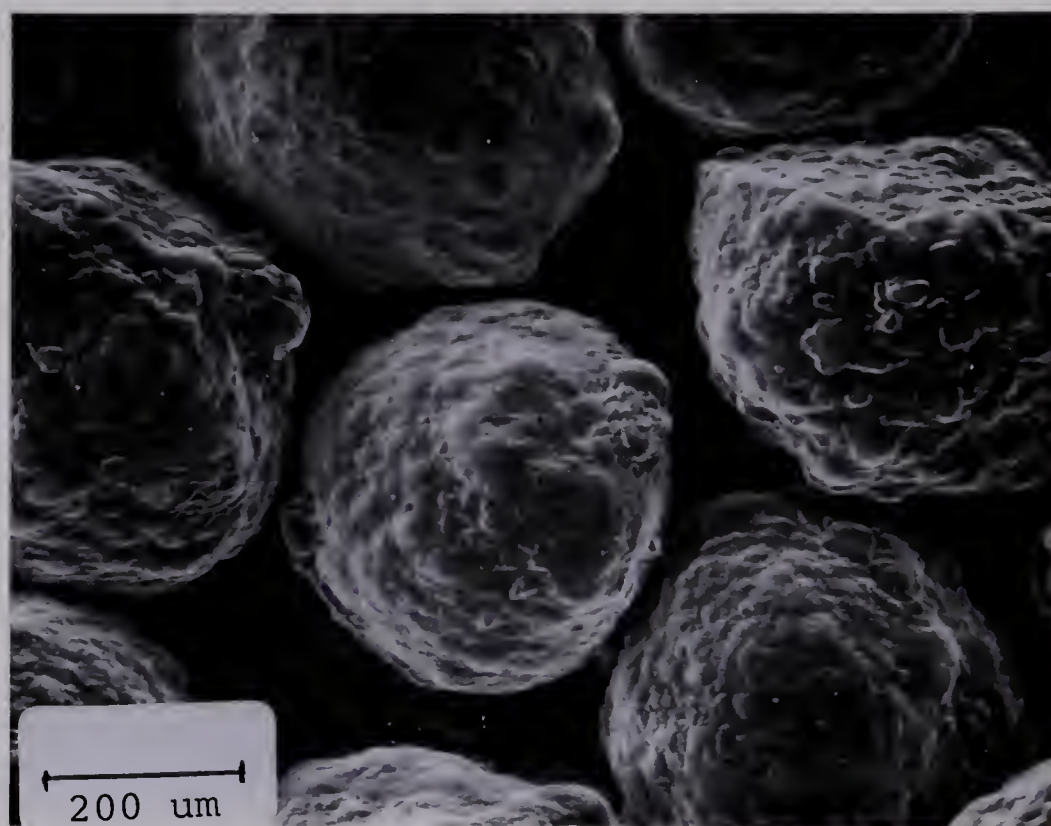


Figure 8. Electron Photomicrograph of 42 mesh Coke, 100X.

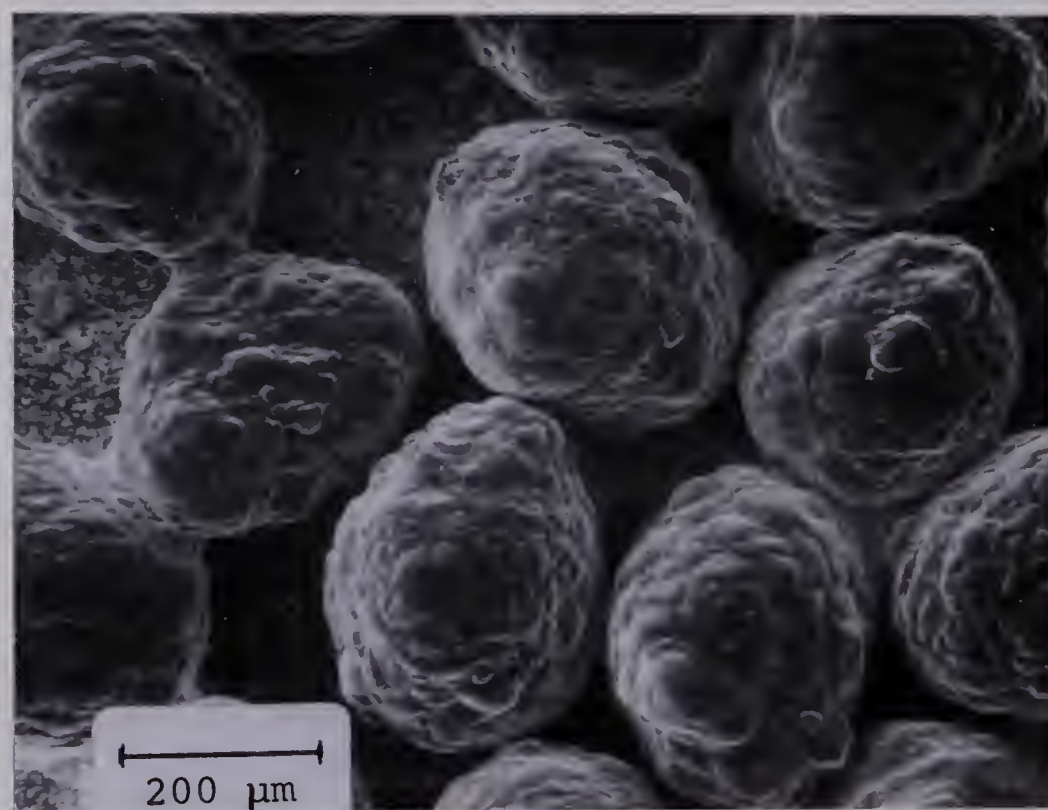


Figure 9. Electron Photomicrograph of 60 mesh Coke, 100X.

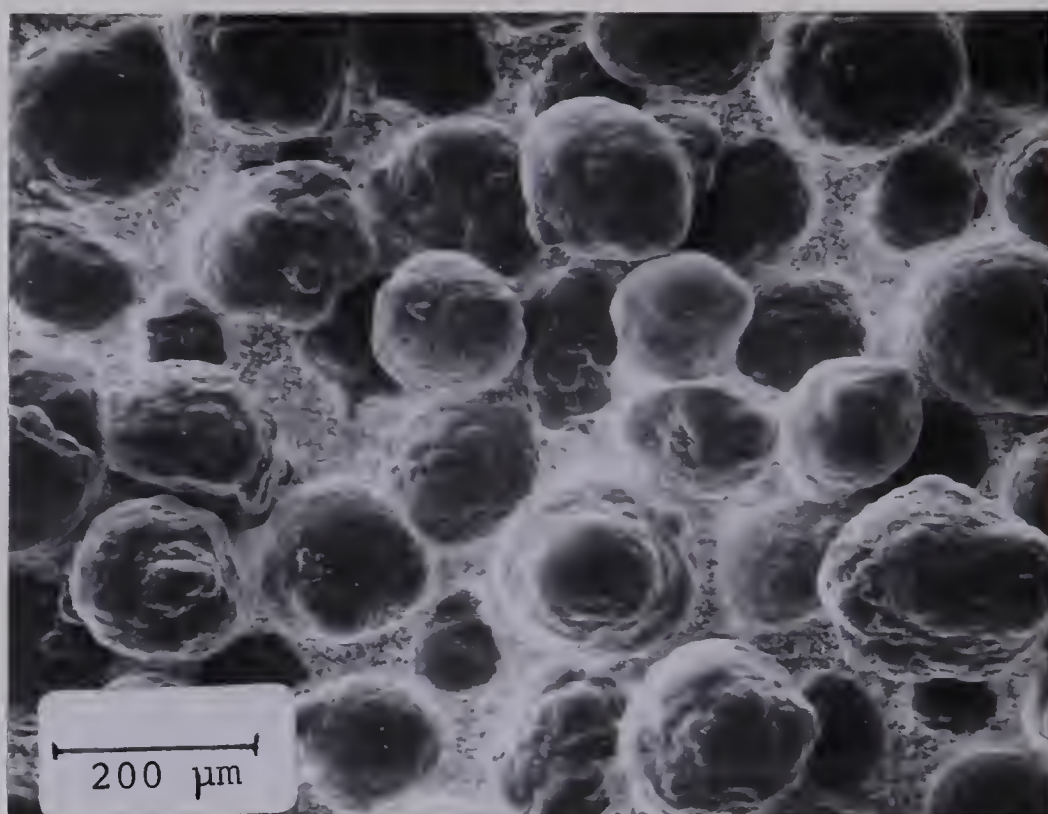


Figure 10. Electron Photomicrograph of 100 mesh Coke, 100X.

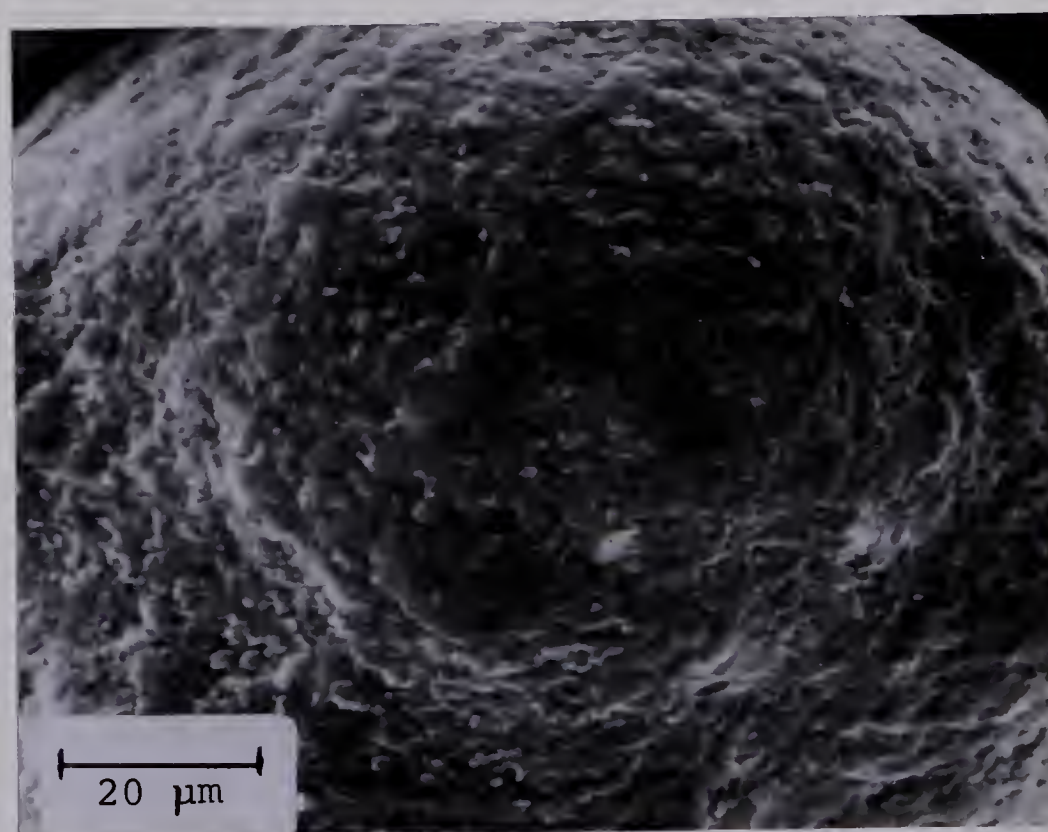


Figure 11. Electron Photomicrograph of 100 mesh Coke, 1000X.

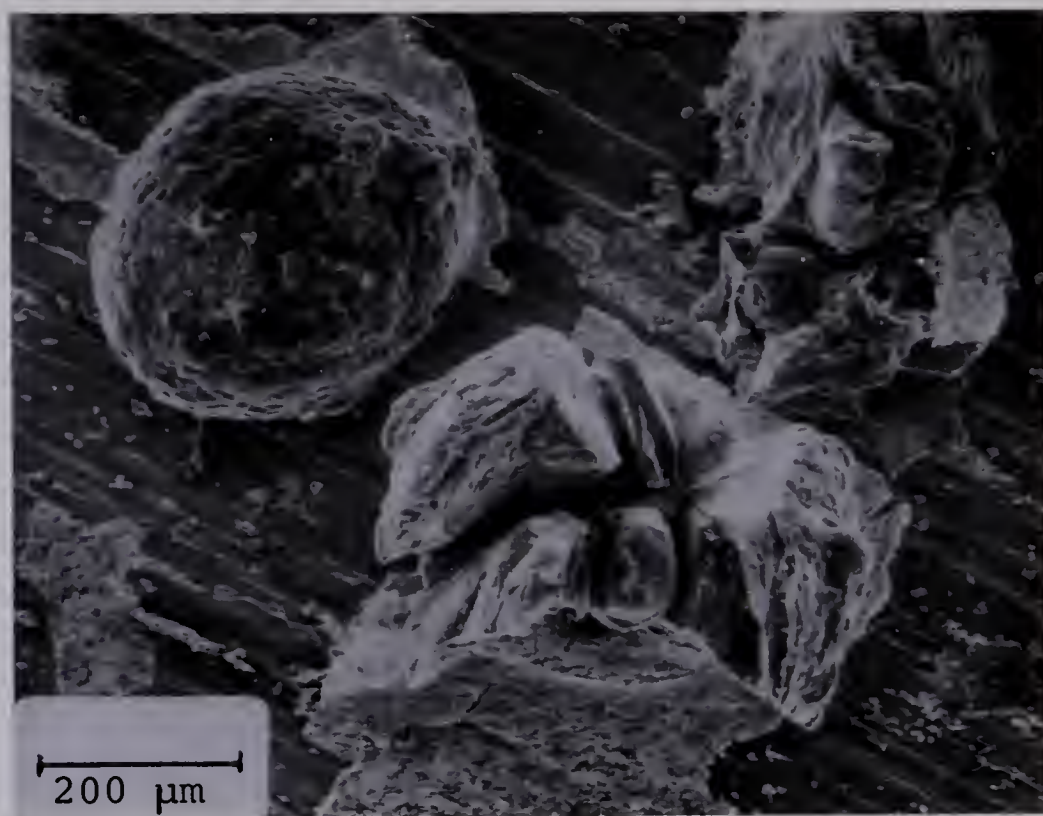


Figure 12. Electron Photomicrograph of Fractured 42 mesh Coke, 100X.

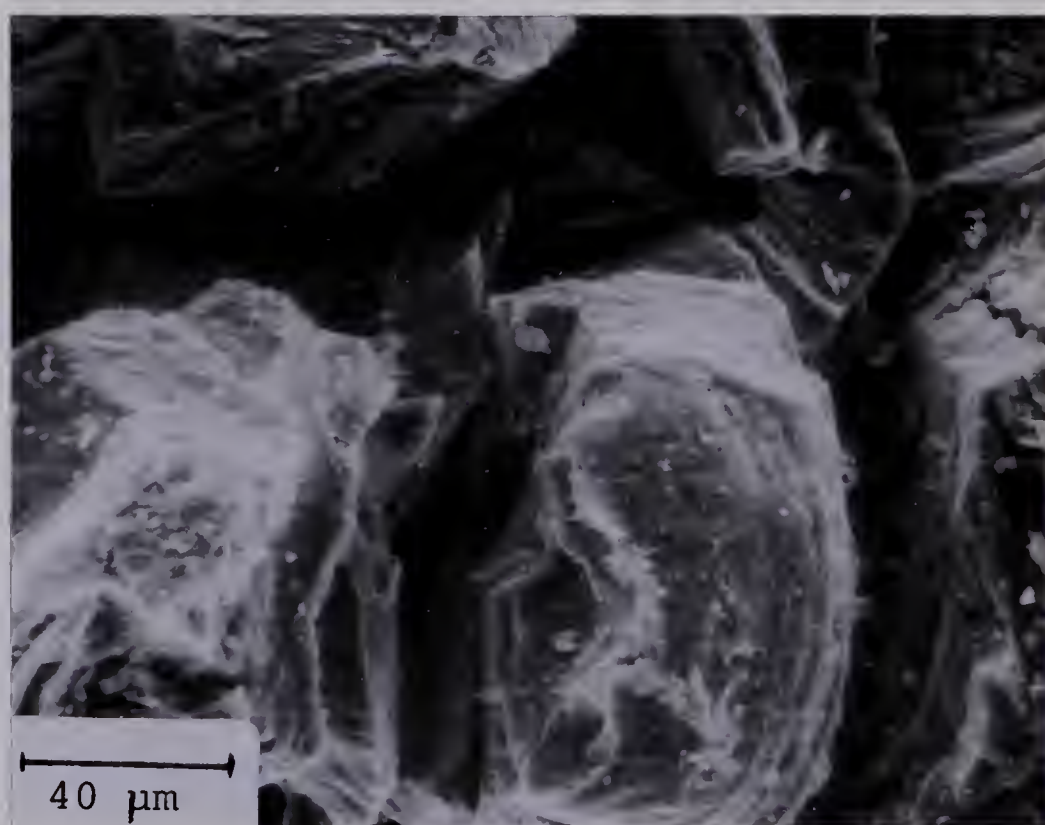


Figure 13. Electron Photomicrograph of Fractured 42 mesh Coke, 500X.

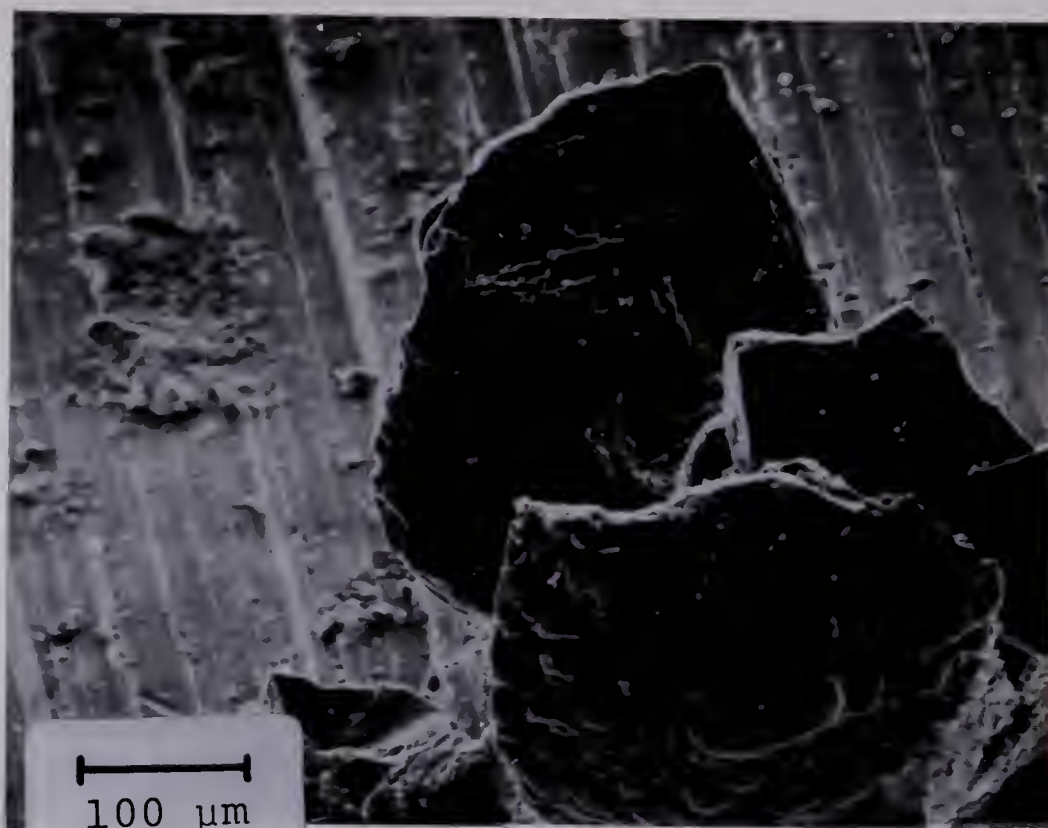


Figure 14. Electron Photomicrograph of Fractured 42 mesh Coke, 150X.

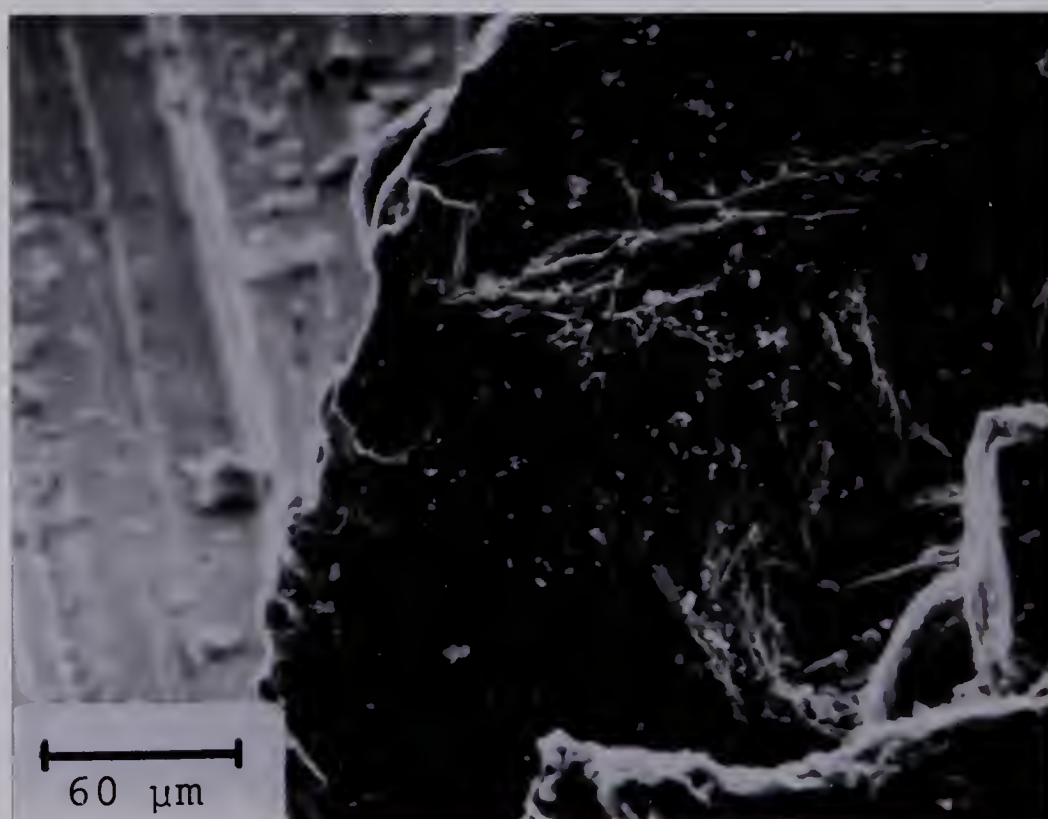


Figure 15. Electron Photomicrograph of Fractured 42 mesh Coke, 300X.

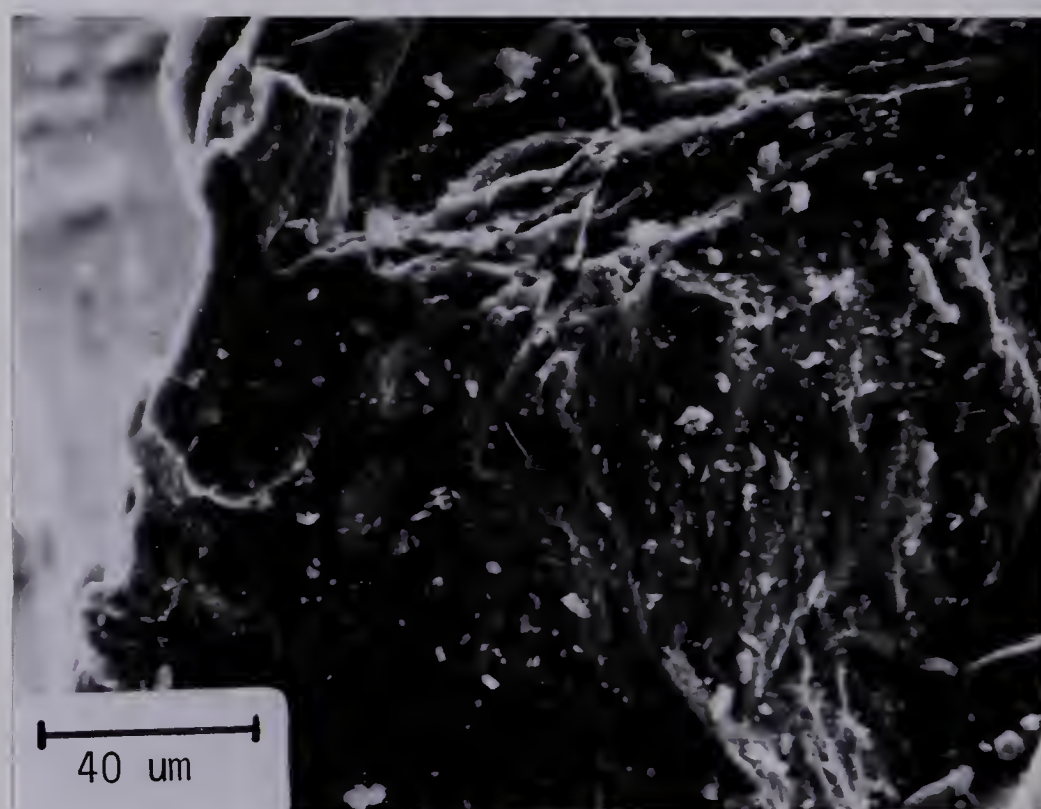


Figure 16. Electron Photomicrograph of Fractured 42 mesh Coke, 500X.



Figure 17. Electron Photomicrograph of Ash from 60 mesh Coke, 90X.



Figure 18. Electron Photomicrograph of Ash from 60 mesh Coke, 470X.



Figure 19. Electron Photomicrograph of Ash from 42 mesh Coke, 100X.



Figure 20. Electron Photomicrograph of Ash from 42 mesh Coke, 520X.



Figure 21. Electron Photomicrograph of Partially Oxidized 60 mesh Coke Ashed for 24 hours, 300X.



Figure 22. Electron Photomicrograph of Partially Oxidized 60 mesh Coke Ashed for 48 hours, 300X.

structure of the low temperature ashed coke particles is less disturbed. Hence, this gives more evidence to confirm that the growth of fluid coke particles in the fluid coker is by deposition of material onto their surfaces.

When the fractured coke particles were observed under the scanning electron microscope, the energy dispersive x-ray analyzer was used to locate any particularly high sulphur content regions inside the particles. The existence of a high sulphur content area implies the presence of a mineral sulphur crystal, such as iron sulphide. However, no such structure was found inside the coke particles. This suggests that most of the sulphur exists in organic forms.

7. Multi-elemental Analysis of the Fluid Coke Ash

Similar to coal, Syncrude fluid coke is a fairly 'dirty' fuel compared to liquid fuels because after combustion, 7 to 8 wt % of material remains in the form of coke ash. Hence, it is important to monitor the inorganic constituents in the fluid coke during various stages of its preparation and utilization.

Since the mineral matter in the fluid coke may be an intrinsic catalyst for its gasification, the nature of the coke ash should be determined prior to a study of the gasification process. Also, in a high temperature environment, some elements (e.g. vanadium and nickel) are corrosive. Hence it is essential to know the concentration of various inorganic elements in the ash.

There are some fundamental distinctions between the mineral matter in the fluid coke and the ash produced from high temperature ashing. During the course of combustion at temperatures above 600° C, carbon dioxide from the mineral carbonates and the water of hydration from hydrated silicates are lost. Also, sulphides are oxidized to oxides. As a result of dehydration, decomposition, oxidation and partial loss of volatile constituents such as Na, Cl and Hg, the high temperature ash is qualitatively and quantitatively different from the mineral matter that gave rise to it.

Several attempts were made to ash the fluid coke using the low temperature ashing method as it alters very little the nature of the mineral matter. It was, however, not successful because it took too much time for complete ashing. It required more than 3 or 4 days to ash a few grams of coke completely. Hence, all of the samples for multi-elemental analysis were prepared by the high temperature ashing method.

At the beginning of the research there were several available choices of analytical methods, namely neutron activation analysis (N.A.A.), atomic absorption spectroscopy (A.A.S.) and inductively coupled plasma emission spectroscopy (I.C.P.) . Some trial analyses were done with these three analytical methods. Finally, only atomic absorption spectroscopy and inductively coupled plasma emission spectroscopy were adopted for the entire analytical analysis. The reasons for rejecting neutron activation analysis were its excessive time requirements and the availability of neutron activation facilities for only four hours per week². In addition, the lengthy half-lives of some elements necessitate several days for their detections after irradiation of the sample. Hence, it was not possible to do the multi-elemental analysis by neutron activation, despite its high sensitivity and selectivity.

²N.A.A. is located at the Slowpoke Nuclear Reactor Centre, Faculty of Pharmacy, University of Alberta.

7.1 Experimental Procedure

7.1.1 Preparation of Ash Samples

About 2 to 3 grams of a coke sample were weighed to the nearest 0.1 mg in a porcelain combustion boat. The sample was then placed in a tube furnace for ashing. It was gradually heated to 300° C for an hour, then to 500° C for a further hour, and finally to 800±10° C for 4 to 5 hours. The reason for not ashing the coke sample rapidly was to avoid any mechanical loss due to rapid expulsion of volatile matter. After ashing, it was cooled to room temperature and again weighed to the nearest 0.1 mg. 2 to 3 grams of a coke sample should yield about 0.2 gram of ash. This ashing procedure, which required a day for completion, should yield a constant weight loss for nominally identical coke samples.

7.1.2 Dissolution of Ash

The method for dissolution of the ash was an acid digestion technique [1,2].

Parr Teflon lined acid digestion bombs Model 4745 were used for the ash dissolution. Each acid digestion bomb consists of a 23 ml Teflon crucible and a stainless steel body. The ash sample previously prepared by high temperature ashing was quantitatively transferred from the porcelain

combustion boat to the Teflon crucible. Wetting of the sample with 2.0 ml of aqua regia was followed by the addition of 3.0 ml of concentrated (48%) hydrofluoric acid. The Teflon crucible was enclosed in the stainless steel body and transferred to a 110° C furnace for 90 minutes. After heating, it was cooled to room temperature. The contents of the Teflon crucible were transferred to a Teflon beaker, with the aid of a Teflon stirring rod. The Teflon crucible was then rinsed with 10 ml of distilled water; 2 grams of boric acid were added to the Teflon beaker to neutralize the excess hydrofluoric acid. Since the dissolution reaction of boric acid is exothermic and the solubility of boric acid is low but increases with temperature, the amount of distilled water added to the beaker was kept to a minimum so that the process for dissolution could be hastened. If precipitates were present, the solution had to be heated on a steam bath until a clear solution resulted. The solution was then transferred to a 100 ml volumetric flask and diluted to volume. After dilution, the solution was immediately transferred to a polyethylene bottle to prevent attack of the volumetric flask by the fluoride solution. The bottles were stored for subsequent analyses. Usually, the solutions were stable for several weeks.

Several attempts were made to digest the coke particles directly without ashing, but they were not successful, despite the use of higher temperatures and excess aqua

regia. The incomplete dissolution of the coke particles may have been caused by the large quantity of organic matter.

7.1.3 Atomic Absorption Spectroscopy

The atomic absorption spectrometer used in the elemental analysis was a Unicam SP1950 Atomic Absorption Spectrophotometer.

Both analytical curve (calibration graph) and standard additions methods were used for elemental analysis. In the method of standard additions, varying amounts of standard were added to a series of solutions containing constant amount of sample [3]. The advantage of the method of standard additions is the elimination of interference from the solution matrix. The method of analytical curve is advantageous because it is less time consuming, provided that the influence of the solution matrix is very small.

The standard solutions were prepared from certified atomic absorption standard reference solutions supplied by the Fisher Scientific Company.

Four elements, nickel, vanadium, iron and titanium, were investigated by both methods of analytical curve and standard additions. For the method of analytical curve, sample solutions were diluted 10-fold for iron and titanium determinations. No dilution was required for nickel and vanadium determinations. For the method of standard

additions, the solutions were adjusted to the range of 0 to 30 ppm for titanium determination and 0 to 20 ppm for iron, nickel and vanadium determinations.

7.1.4 Inductively Coupled Plasma Emission Spectroscopy

The inductively coupled plasma emission spectrometer used in the multi-elemental analysis was a Model 975 made by Jarrell-Ash³.

The method of internal standard calibration was used for multi-elemental analysis. The internal standard was scandium which was not found in the coke ash. An aliquot of each sample solution was diluted 10-fold. 1 ppm scandium was added to it. After dilution, the solution was ready for multi-elemental analysis. A blank was used throughout the analysis containing the same amounts of aqua regia, hydrofluoric acid, and boric acid and was used for the blank correction in the inductively coupled plasma emission spectroscopy measurements. Twenty-one elements were determined. These were Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, P, Pb, Si, Te, Ti, V, Y, Zn and Zr.

³ The I.C.P. spectrometric facility was provided by Sherritt Gordon Mines Ltd., Fort Saskatchewan, Alberta, Canada.

7.2 Results and Discussion

The batches of Dec 7, '78 and Aug 12, '80 were selected for the multi-elemental analysis. They were chosen because the former batch had the largest variation in ash content (6.95 % to 8.21 %) and the latter had the least variation (8.16% to 8.49 %) (Table 13). Duplicates of each particle size range for both batches were prepared for elemental analysis using atomic absorption spectroscopy and inductively coupled emission spectroscopy.

The analysis done by atomic absorption spectroscopy showed that the results obtained by the method of analytical curves were higher than those determined by the method of standard additions. Iron concentration was higher by 5 %, vanadium by 10 %, nickel by 20 % and titanium by 400 %. This phenomenon was quite understandable as the sample solutions contained 30 to 40 different elements capable of causing substantial interference. The solution matrix effect was particularly prominent for titanium because the absorbance of a titanium solution is greatly enhanced in the presence of fluoride and iron.

On comparison of the analyses obtained by atomic absorption spectroscopy using the method of standard addition with those obtained by inductively coupled plasma emission spectroscopy, it was found that determinations of iron, nickel, titanium and vanadium agreed within 2%. This

indicates that the method of inductively coupled plasma spectroscopy is relatively free from interference caused by the solution matrix. Hence, inductively coupled plasma emission spectroscopy is superior to the method of analytical curve by using atomic absorption spectroscopy for multi-elemental analysis of coke and similar materials.

Since inductively coupled plasma emission spectroscopy is capable of determining several elements simultaneously while atomic absorption is restricted to a single element at a time, the former method becomes more attractive for multi-elemental analysis. Hence, most of the elemental analysis in this research was accomplished with inductively coupled plasma emission spectroscopy.

From analysis by using inductively coupled plasma emission spectroscopy, the major elements in the coke ash were found to be Al, Ca, Fe, Mg, Mn, Ni, Si, Ti, and V. The concentrations of these elements in the coke ash were approximately equal to or in excess of 1 wt % . The minor elements (trace elements) were As, Cd, Co, Cr, Cu, P, Pb, Te, Y, Zn and Zr; their concentrations in the coke were less than 50 ppm.

Originally, all the elemental analyses were reported in terms of weight percent of coke (Tables 18-26) and their concentrations were plotted as a function of particle size (Figures 23-40). All the plots, except the Aug 12, '80 iron,

manganese and titanium plots (Figures 28, 32 and 38), show a common trend which indicates that the smaller particle ranges had higher concentrations of the major elements. This phenomenon could be explained by the fact that the smaller particles had higher ash content (Table 13 and Figure 4). However, this explanation is based on an assumption that the quality of the coke ash produced from different particle size ranges was the same. In other words, the concentrations of the major elements in the coke ash should have been constant. If this is true, then plots of the concentrations of major elements as weight percent of ash versus particle size (Figures 41-58) should yield approximately horizontal lines. Nevertheless, not all elements behaved ideally. In addition to iron, manganese and titanium of Aug 12, '80 (Figures 28, 32 and 28), nickel and vanadium of Dec 8, '78 (Figures 51, 57) showed a reverse trend which indicates that the larger particle size ranges contain a higher concentration of these elements. Hence, this confirms that nickel and vanadium are associated with organic matter. Also, the batch of Aug 12, '80 had the lowest ash content in the particle size range of 150 to 300 microns and it was found that nickel and vanadium had their highest concentration in this range. These finding implies that nickel and vanadium should be associated with the organic matter in the coke.

The concentrations of iron, manganese and titanium in the ash of the Dec 8, '78 batch (Figures 27, 31 and 37) did not have the same trend as those in the Aug 12, '80 batch. Hence, their affiliation with organic matter is unresolved. Furthermore, in the batch of Dec 7, '78, the concentration of iron in the ash was constant (Figure 27) and that of titanium was higher in the smaller particles (Figure 37). For the rest of the major elements, especially aluminum and silicon, their concentrations in the ash were higher in the smaller particles, rather than being constant over the full range of particle sizes.

All elemental analyses (Tables 18 -35) are reported on an as received basis. In terms of accuracy, most of the major elements had relative errors less than 1 % which is typical for the performance of inductively coupled plasma emission spectroscopy. This also demonstrates that fluid coke of any particular particle size range is quite homogeneous.

Table 18. Concentration of Aluminum in Fluid Coke.

<u>Particle Size</u> <u>(Mesh)</u>	<u>Dec 7, '78</u> <u>(wt %)</u>	<u>Aug 12, '80</u> <u>(wt %)</u>
200	1.18±0.00	1.23±0.00
170	1.19±0.00	1.23±0.01
150	1.17±0.00	1.21±0.01
115	1.15±0.01	1.21±0.00
100	1.10±0.00	1.19±0.00
80	1.05±0.00	1.18±0.00
65	1.03±0.00	1.18±0.00
60	0.996±0.002	1.16±0.00
48	0.975±0.001	1.14±0.01
42	0.958±0.008	1.12±0.00

Table 19. Concentration of Calcium in Fluid Coke.

<u>Particle Size</u> <u>(Mesh)</u>	<u>Dec 7, '78</u> <u>(wt %)</u>	<u>Aug 12, '80</u> <u>(wt %)</u>
200	0.325±0.001	0.171±0.005
170	0.328±0.003	0.174±0.002
150	0.317±0.002	0.172±0.005
115	0.314±0.001	0.173±0.000
100	0.301±0.006	0.165±0.003
80	0.288±0.002	0.167±0.001
65	0.287±0.003	0.167±0.001
60	0.282±0.001	0.164±0.001
48	0.279±0.004	0.166±0.001
42	0.282±0.001	0.160±0.000

Table 20. Concentration of Iron in Fluid Coke.

<u>Particle Size</u>	<u>Dec 7, '78</u>	<u>Aug 12, '80</u>
<u>(Mesh)</u>	<u>(wt %)</u>	<u>(wt %)</u>
200	0.472±0.000	0.566±0.001
170	0.474±0.004	0.569±0.003
150	0.464±0.001	0.572±0.004
115	0.455±0.001	0.576±0.003
100	0.438±0.003	0.583±0.002
80	0.422±0.001	0.588±0.000
65	0.419±0.003	0.597±0.001
60	0.407±0.001	0.600±0.002
48	0.409±0.002	0.609±0.001
42	0.408±0.003	0.615±0.001

Table 21. Concentration of Magnesium in Fluid Coke.

<u>Particle Size</u> <u>(Mesh)</u>	<u>Dec 7, '78</u> <u>(ppm)</u>	<u>Aug 12, '80</u> <u>(ppm)</u>
200	749±0	828±0
170	754±3	829±1
150	732±6	818±5
115	722±2	819±3
100	693±7	807±4
80	665±5	802±1
65	651±5	802±0
60	631±2	792±1
48	622±6	785±2
42	617±0	777±2

Table 22. Concentration of Manganese in Fluid Coke.

<u>Particle Size</u> <u>(Mesh)</u>	<u>Dec 7, '78</u> <u>(ppm)</u>	<u>Aug 12, '80</u> <u>(ppm)</u>
200	136±0	161±1
170	137±1	164±1
150	133±1	166±1
115	131±0	167±1
100	126±2	169±1
80	123±0	171±1
65	122±1	172±1
60	120±0	175±2
48	126±2	174±1
42	118±1	174±1

Table 23. Concentration of Nickel in Fluid Coke.

<u>Particle Size</u> <u>(Mesh)</u>	<u>Dec 7, '78</u> <u>(ppm)</u>	<u>Aug 12, '80</u> <u>(ppm)</u>
200	712±0	565±1
170	718±2	562±4
150	718±5	560±8
115	719±3	565±5
100	703±3	560±5
80	685±2	556±10
65	676±2	561±6
60	667±2	555±3
48	673±1	549±3
42	658±2	548±3

Table 24. Concentration of Silicon in Fluid Coke.

<u>Particle Size</u> <u>(Mesh)</u>	<u>Dec 7, '78</u> <u>(wt %)</u>	<u>Aug 12, '80</u> <u>(wt %)</u>
200	1.59±0.07	1.83±0.04
170	1.61±0.08	1.83±0.05
150	1.58±0.07	1.82±0.03
115	1.55±0.06	1.81±0.04
100	1.48±0.05	1.80±0.04
80	1.35±0.01	1.77±0.05
65	1.34±0.01	1.77±0.05
60	1.29±0.01	1.74±0.06
48	1.30±0.01	1.75±0.05
42	1.35±0.01	1.75±0.05

Table 25. Concentration of Titanium in Fluid Coke.

<u>Particle Size</u> <u>(Mesh)</u>	<u>Dec 7, '78</u> <u>(ppm)</u>	<u>Aug 12, '80</u> <u>(ppm)</u>
200	1453±1	1484±1
170	1448±5	1484±3
150	1427±3	1554±13
115	1398±0	1570±1
100	1369±6	1617±3
80	1347±6	1656±4
65	1335±4	1668±26
60	1318±9	1695±29
48	1301±8	1714±22
42	1288±8	1730±43

Table 26. Concentration of Vanadium in Fluid Coke.

<u>Particle Size</u> <u>(Mesh)</u>	<u>Dec 7, '78</u> <u>(ppm)</u>	<u>Aug 12, '80</u> <u>(ppm)</u>
200	1921±3	1535±4
170	1947±10	1541±3
150	1932±6	1534±7
115	1923±4	1541±5
100	1883±6	1539±5
80	1850±4	1535±1
65	1837±8	1540±0
60	1815±5	1530±2
48	1808±1	1525±2
42	1792±8	1518±1

Table 27. Concentration of Aluminum in Fluid Coke Ash.

<u>Particle Size</u> <u>(Mesh)</u>	<u>Dec 7, '78</u> <u>(wt %)</u>	<u>Aug 12, '80</u> <u>(wt %)</u>
200	14.7±0.0	14.7±0.1
170	14.8±0.1	14.7±0.1
150	14.6±0.0	14.6±0.1
115	14.8±0.1	14.6±0.1
100	14.6±0.1	14.5±0.0
80	14.5±0.0	14.5±0.0
65	14.5±0.1	14.4±0.1
60	14.3±0.0	14.3±0.1
48	14.1±0.1	14.0±0.1
42	13.6±0.1	13.6±0.0

Table 28. Concentration of Calcium in Fluid Coke Ash.

<u>Particle Size</u>	<u>Dec 7, '78</u>	<u>Aug 12, '80</u>
<u>(Mesh)</u>	<u>(wt %)</u>	<u>(wt %)</u>
200	4.06±0.01	2.04±0.04
170	4.08±0.03	2.08±0.03
150	3.96±0.01	2.06±0.06
115	4.02±0.02	2.07±0.00
100	3.99±0.02	1.99±0.03
80	3.98±0.02	2.05±0.02
65	4.05±0.02	2.04±0.00
60	4.05±0.01	2.01±0.01
48	4.03±0.07	2.03±0.04
42	3.99±0.01	1.94±0.00

Table 29. Concentration of Iron in Fluid Coke Ash.

<u>Particle Size</u> <u>(Mesh)</u>	<u>Dec 7, '78</u> <u>(wt %)</u>	<u>Aug 12, '80</u> <u>(wt %)</u>
200	5.88±0.01	6.75±0.02
170	5.89±0.06	6.78±0.02
150	5.80±0.01	6.88±0.06
115	5.83±0.01	6.90±0.03
100	5.82±0.04	7.04±0.02
80	5.83±0.03	7.19±0.01
65	5.90±0.03	7.27±0.03
60	5.84±0.01	7.35±0.01
48	5.88±0.05	7.45±0.03
42	5.76±0.02	7.46±0.02

Table 30. Concentration of Magnesium in Fluid Coke Ash.

<u>Particle Size</u>	<u>Dec 7, '78</u>	<u>Aug 12, '80</u>
<u>(Mesh)</u>	<u>(wt %)</u>	<u>(wt %)</u>
200	0.933±0.003	0.987±0.001
170	0.934±0.004	0.989±0.002
150	0.914±0.004	0.981±0.010
115	0.926±0.004	0.982±0.002
100	0.920±0.010	0.976±0.004
80	0.917±0.006	0.979±0.003
65	0.916±0.005	0.978±0.005
60	0.906±0.001	0.970±0.005
48	0.895±0.007	0.960±0.005
42	0.871±0.004	0.942±0.003

Table 31. Concentration of Manganese in Fluid Coke Ash.

<u>Particle Size</u>	<u>Dec 7, '78</u>	<u>Aug 12, '80</u>
<u>(Mesh)</u>	<u>(wt %)</u>	<u>(wt %)</u>
200	0.169±0.000	0.194±0.001
170	0.170±0.002	0.196±0.000
150	0.166±0.000	0.199±0.002
115	0.168±0.001	0.201±0.001
100	0.168±0.002	0.204±0.001
80	0.169±0.001	0.210±0.002
65	0.172±0.001	0.210±0.001
60	0.171±0.000	0.215±0.004
48	0.180±0.003	0.213±0.001
42	0.167±0.000	0.211±0.001

Table 32. Concentration of Nickel in Fluid Coke Ash.

<u>Particle Size</u>	<u>Dec 7, '78</u>	<u>Aug 12, '80</u>
<u>(Mesh)</u>	<u>(wt %)</u>	<u>(wt %)</u>
200	0.887±0.002	0.673±0.000
170	0.890±0.003	0.671±0.005
150	0.896±0.004	0.674±0.010
115	0.921±0.001	0.679±0.005
100	0.933±0.003	0.677±0.004
80	0.945±0.001	0.680±0.013
65	0.951±0.001	0.684±0.004
60	0.956±0.001	0.680±0.002
48	0.968±0.003	0.672±0.001
42	0.928±0.001	0.664±0.002

Table 33. Concentration of Silicon in Fluid Coke Ash.

<u>Particle Size</u> <u>(Mesh)</u>	<u>Dec 7, '78</u> <u>(wt %)</u>	<u>Aug 12, '80</u> <u>(wt %)</u>
200	19.8±0.9	21.8±0.5
170	20.0±1.0	21.9±0.5
150	19.7±0.9	21.9±0.3
115	19.9±0.7	21.7±0.5
100	19.5±0.6	21.8±0.5
80	18.7±0.1	21.6±0.6
65	18.8±0.1	21.6±1.6
60	18.6±0.2	21.5±0.6
48	18.6±0.0	21.6±0.6
42	19.0±0.1	21.2±0.6

Table 34. Concentration of Titanium in Fluid Coke Ash.

<u>Particle Size</u>	<u>Dec 7, '78</u>	<u>Aug 12, '80</u>
<u>(Mesh)</u>	<u>(wt %)</u>	<u>(wt %)</u>
200	1.81±0.00	1.77±0.00
170	1.80±0.01	1.80±0.00
150	1.78±0.01	1.87±0.01
115	1.79±0.00	1.89±0.01
100	1.82±0.01	1.96±0.01
80	1.86±0.01	2.02±0.00
65	1.88±0.00	2.03±0.04
60	1.89±0.01	2.07±0.03
48	1.87±0.00	2.10±0.03
42	1.81±0.00	2.10±0.02

Table 35. Concentration of Vanadium in Fluid Coke Ash.

<u>Particle Size</u>	<u>Dec 7, '78</u>	<u>Aug 12, '80</u>
<u>(Mesh)</u>	<u>(wt %)</u>	<u>(wt %)</u>
200	2.39±0.01	1.83±0.01
170	2.41±0.01	1.84±0.00
150	2.41±0.00	1.85±0.01
115	2.46±0.01	1.85±0.01
100	2.50±0.01	1.86±0.01
80	2.55±0.01	1.88±0.00
65	2.58±0.01	1.88±0.01
60	2.61±0.01	1.88±0.01
48	2.60±0.01	1.87±0.01
42	2.53±0.01	1.84±0.01

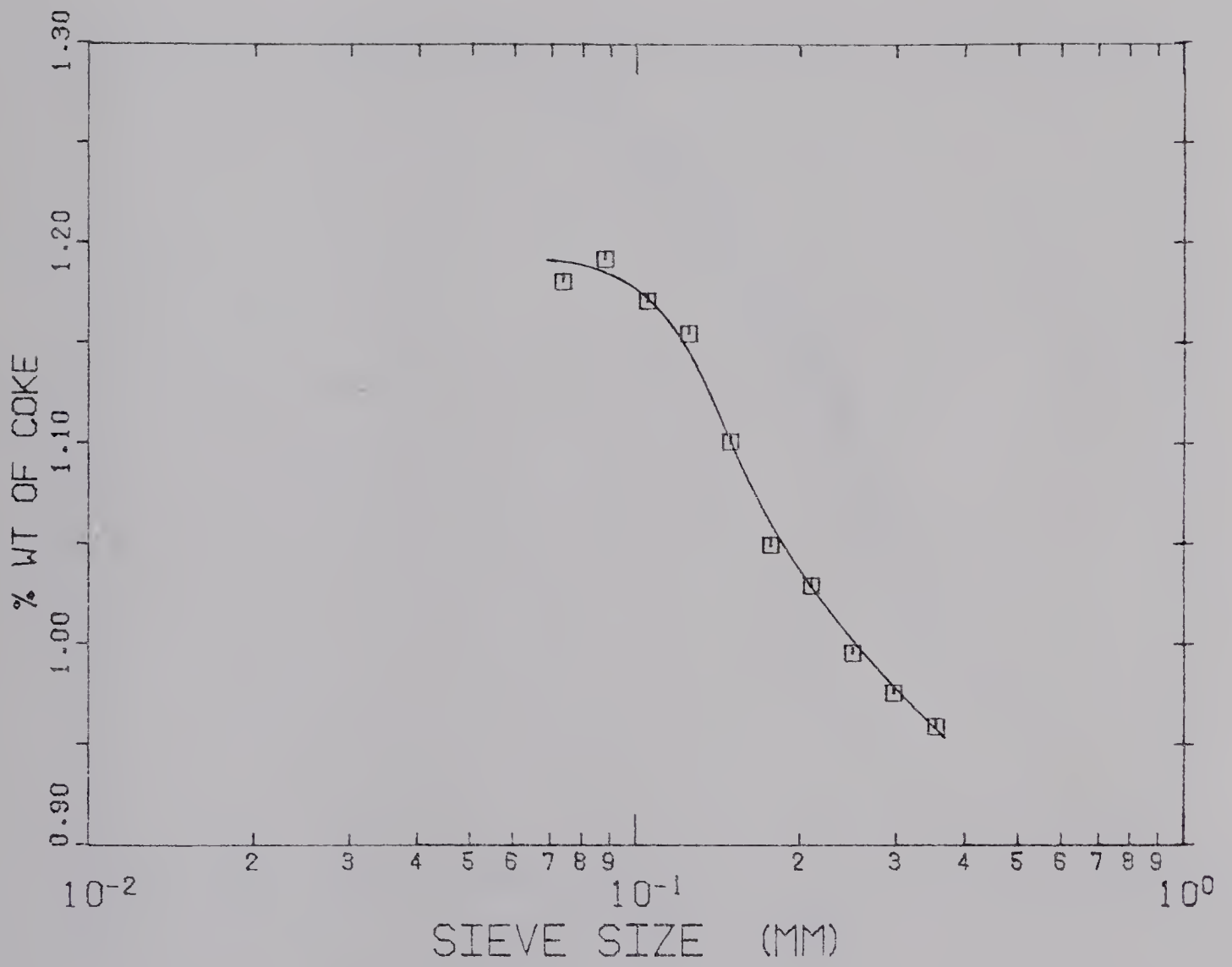


Figure 23. Aluminum Content in Fluid Coke as a Function of Particle Size, Dec 7, '78.

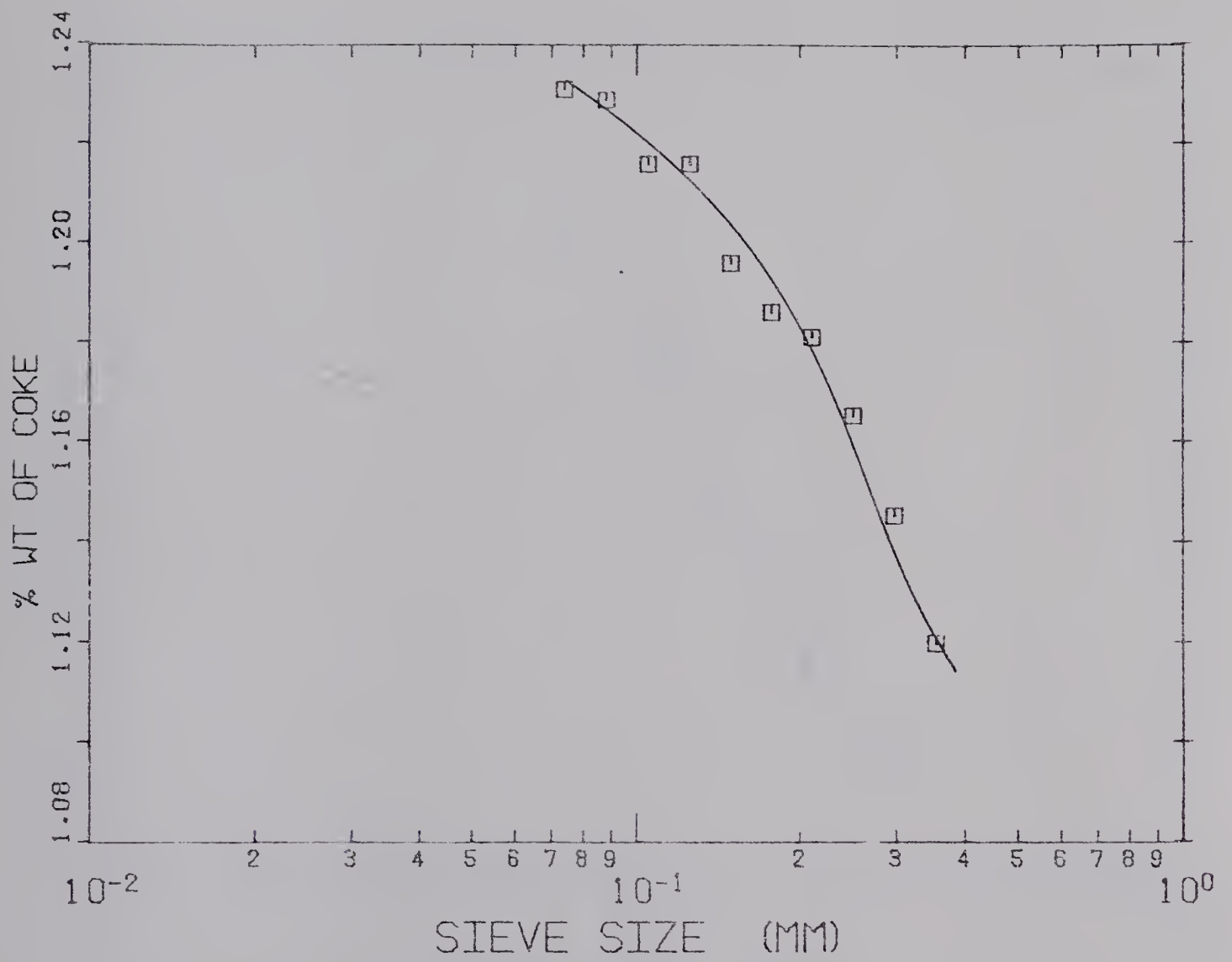


Figure 24. Aluminum Content in Fluid Coke as a Function of Particle Size, Aug 12, '80.

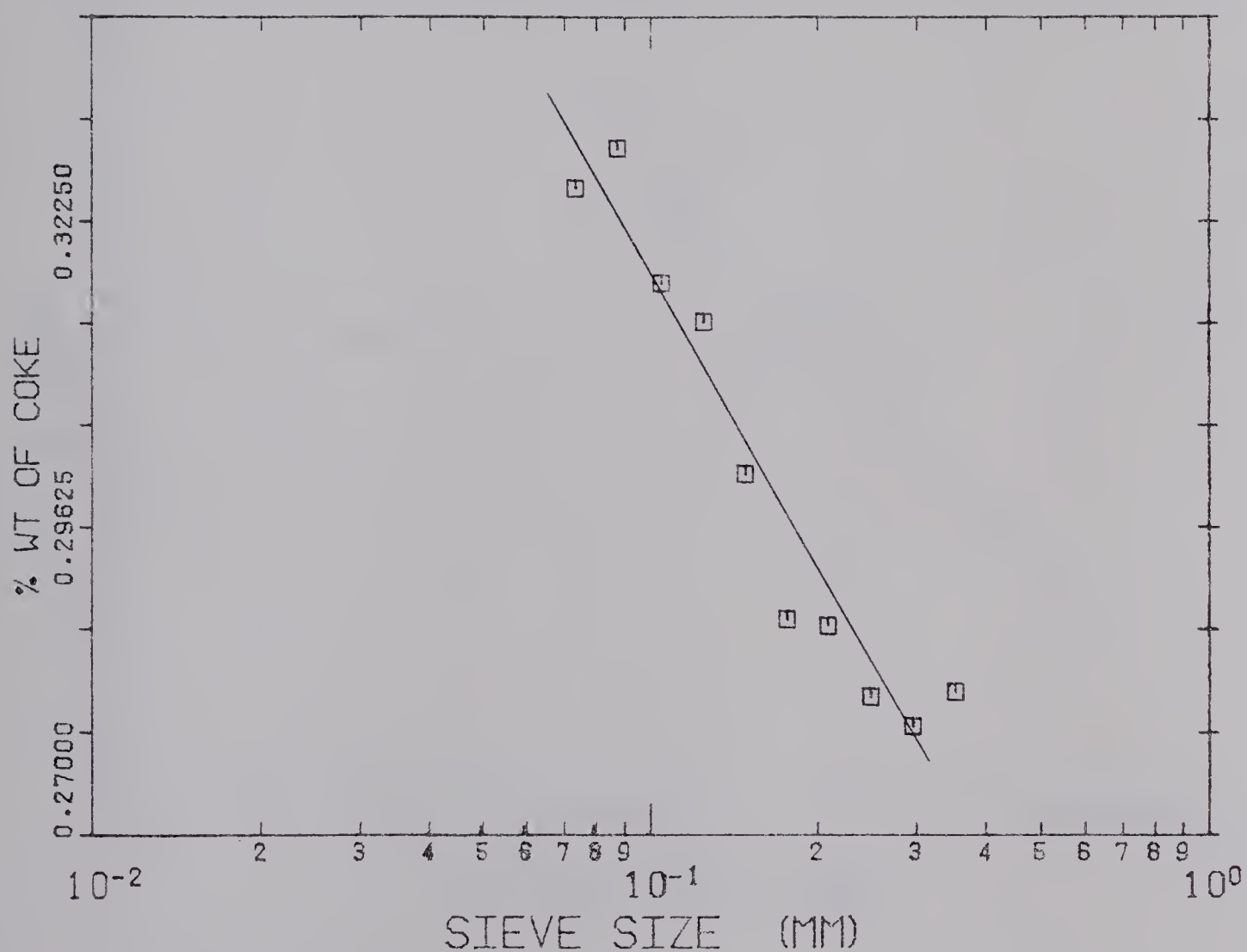


Figure 25. Calcium Content in Fluid Coke as a Function of Particle Size, Dec 7, '78.

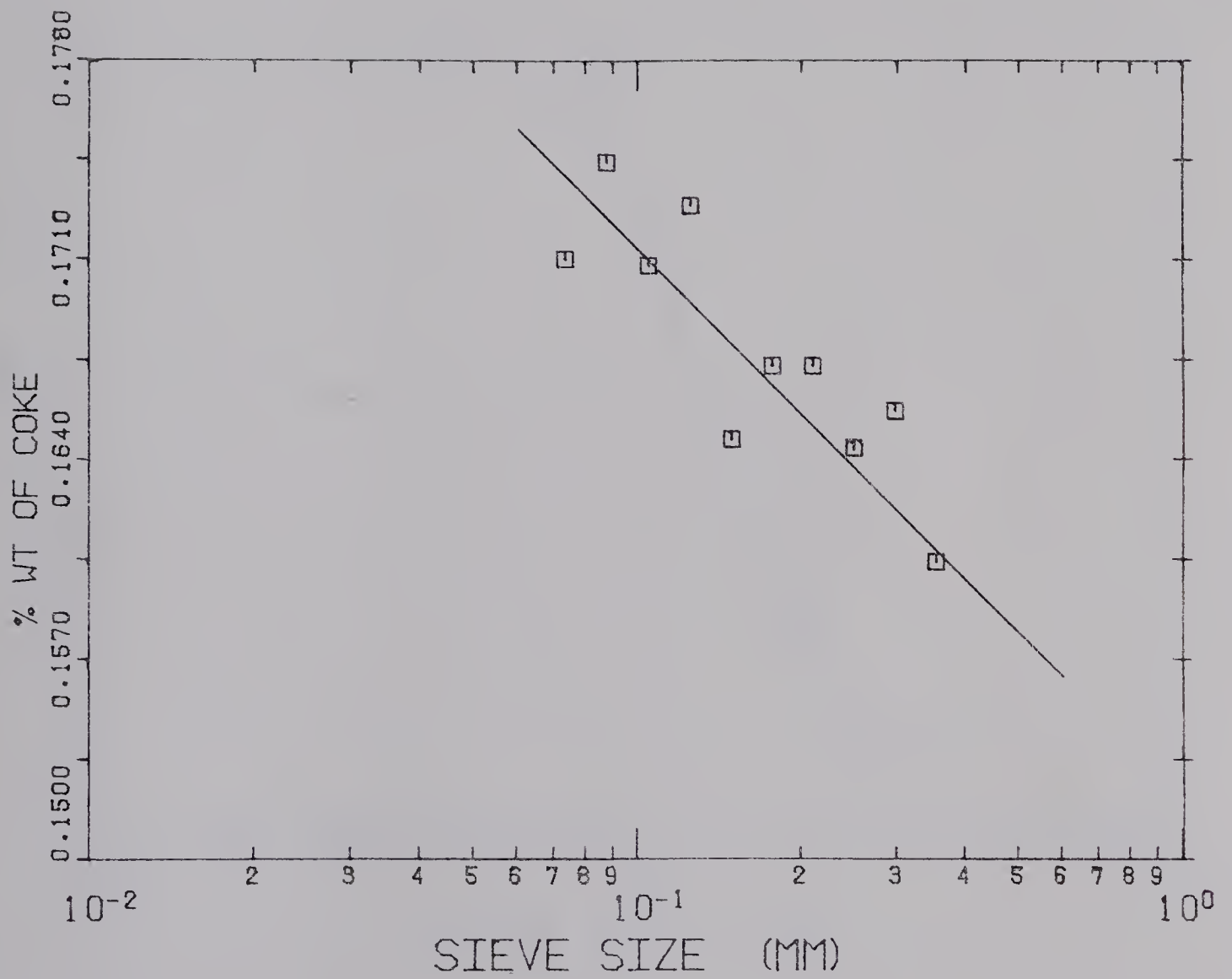


Figure 26. Calcium Content in Fluid Coke as a Function of Particle Size, Aug 12, '80.

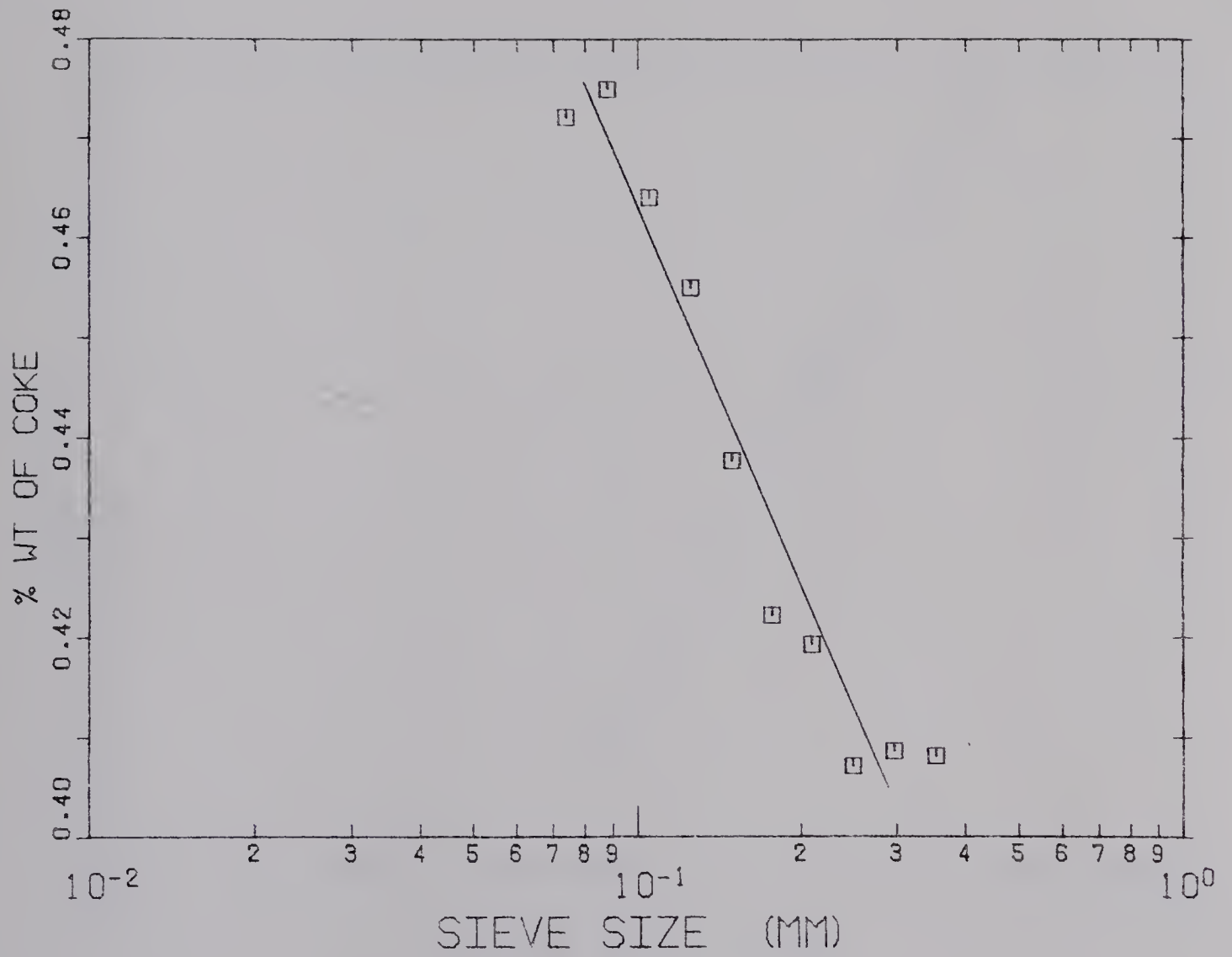


Figure 27. Iron Content in Fluid Coke as a Function of Particle Size, Dec 7, '78.

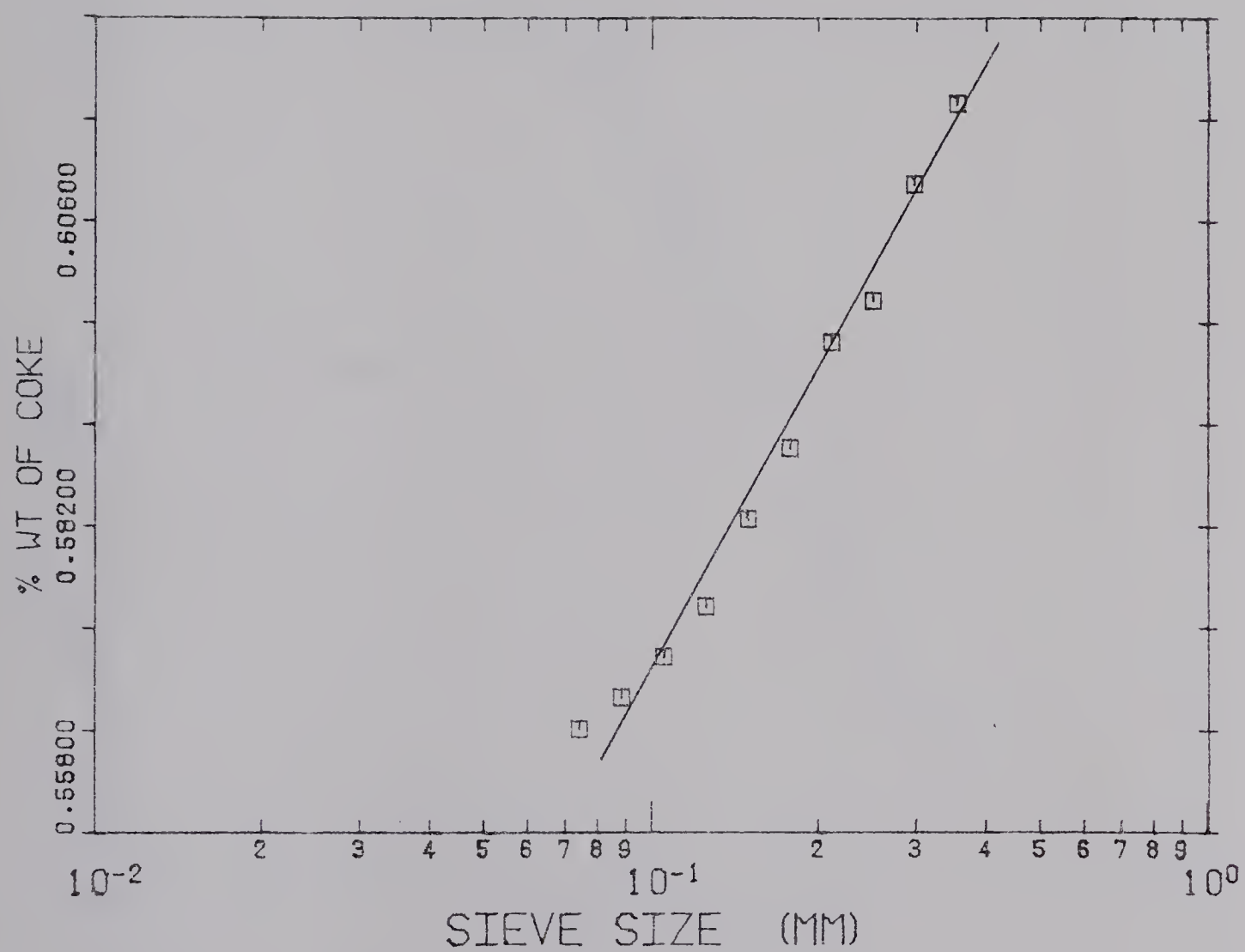


Figure 28. Iron Content in Fluid Coke as a Function of Particle Size, Aug 12, '80.

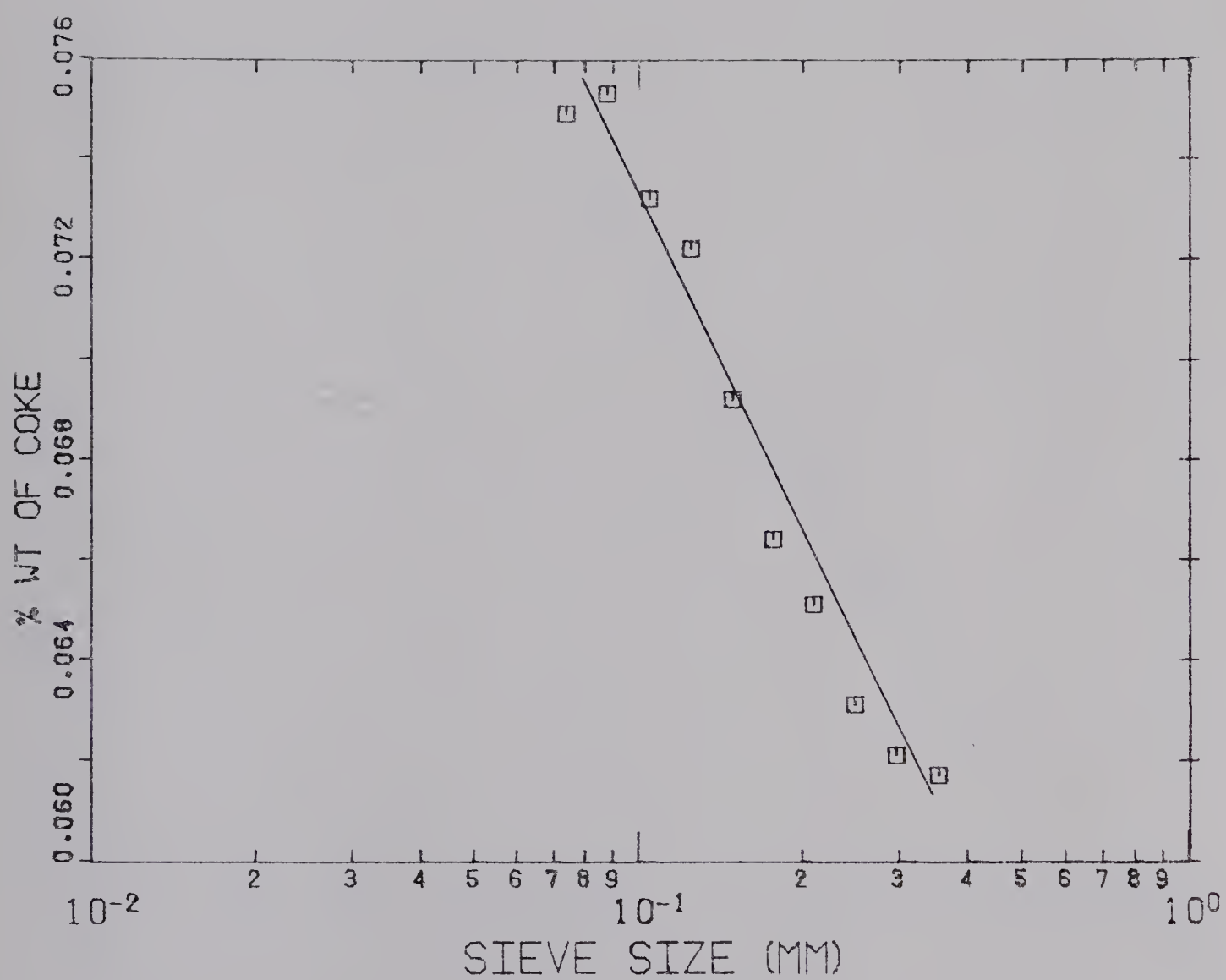


Figure 29. Magnesium Content in Fluid Coke as a Function of Particle Size, Dec 7, '78.

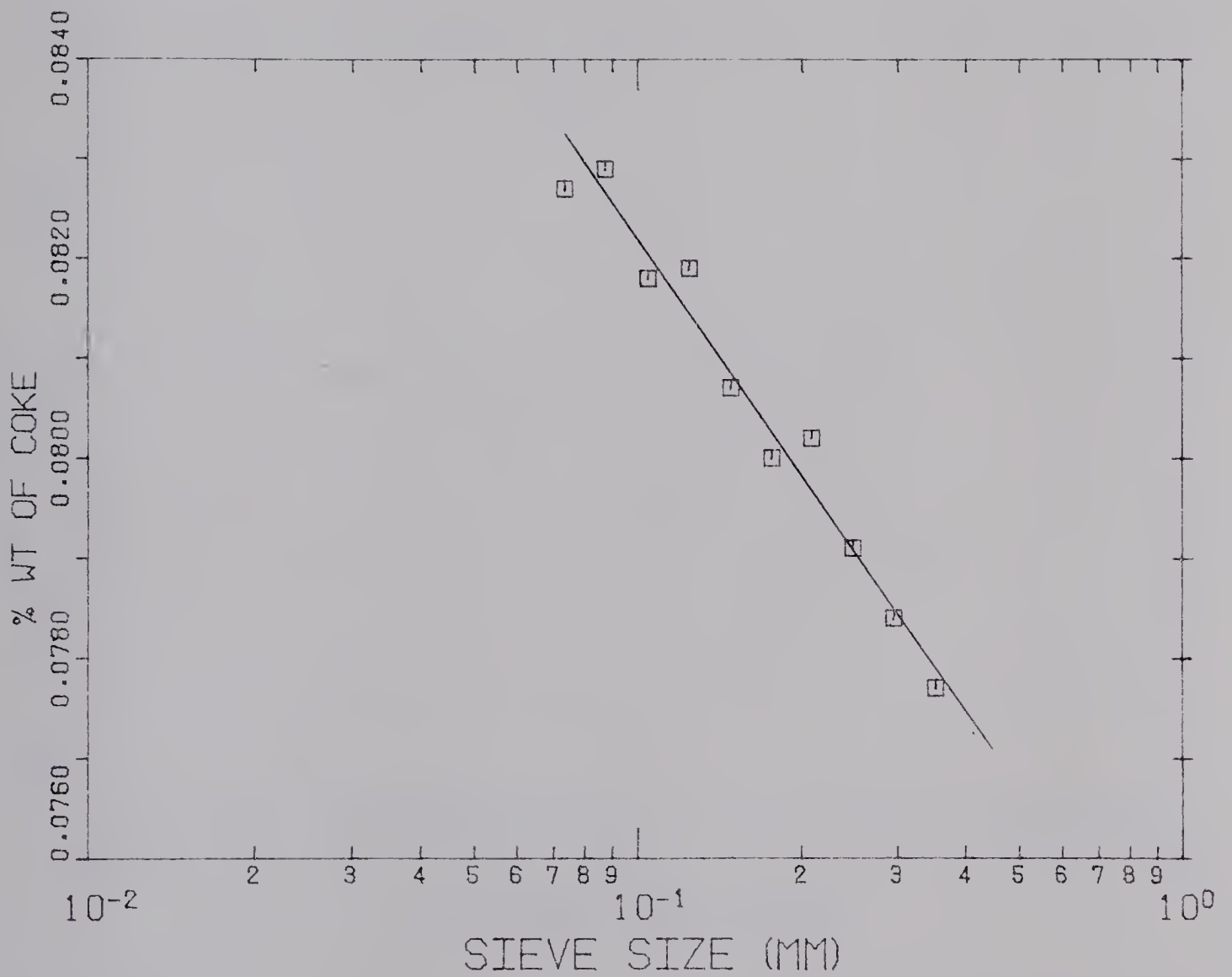


Figure 30. Magnesium Content in Fluid Coke as a Function of Particle Size, Aug 12, '80.

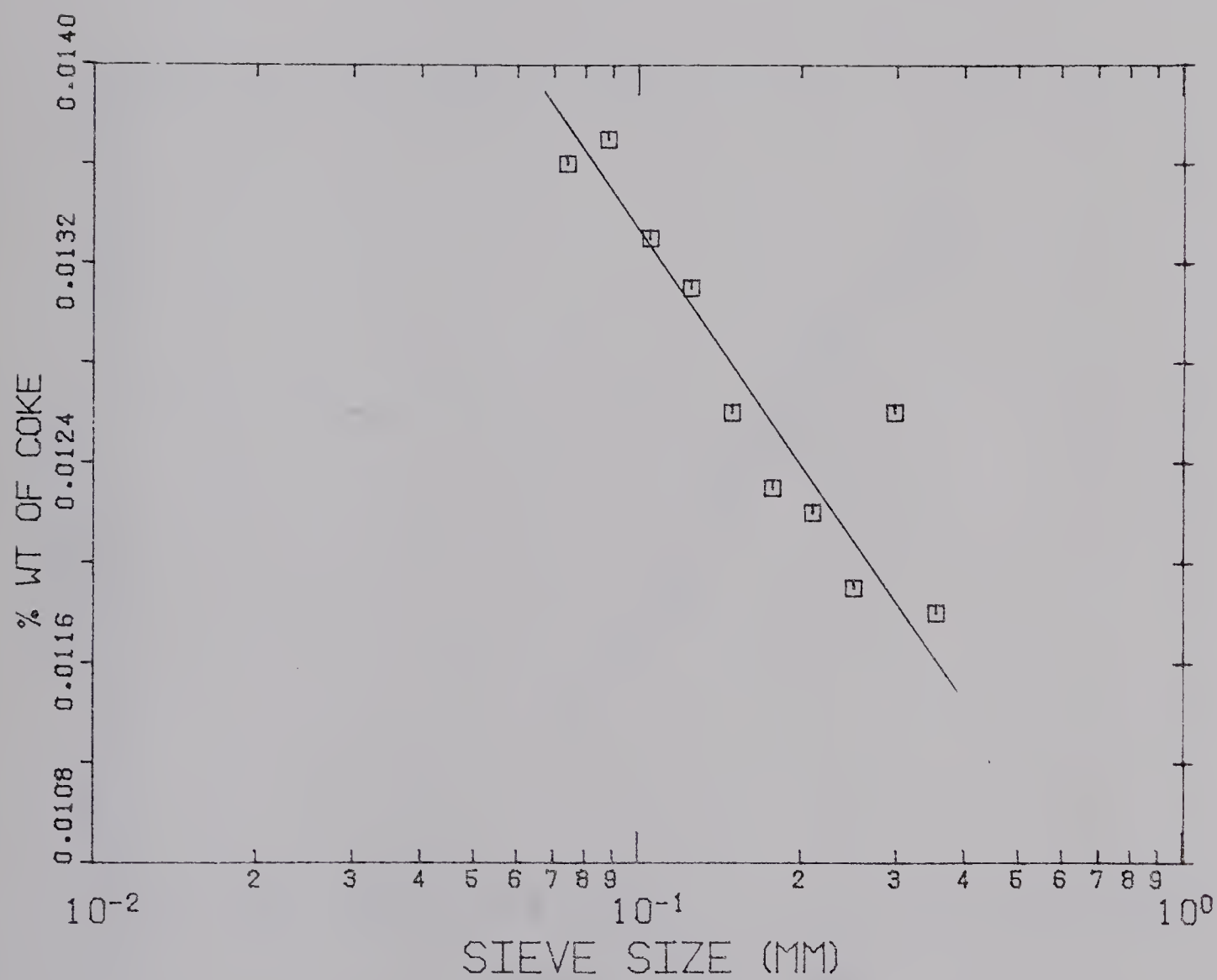


Figure 31. Manganese Content in Fluid Coke as a Function of Particle Size, Dec 7, '78.

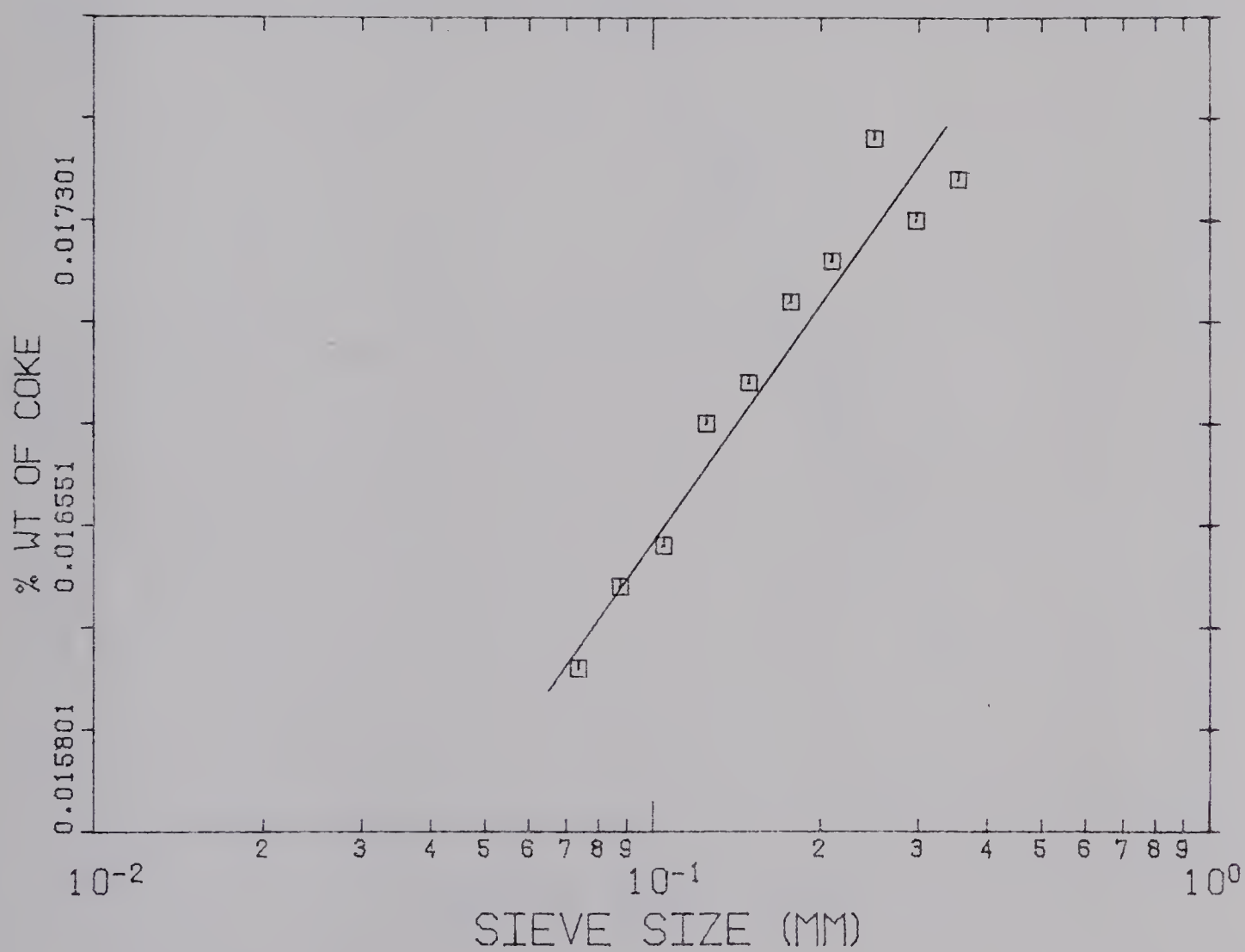


Figure 32. Manganese Content in Fluid Coke as a Function of Particle Size, Aug 12, '80.

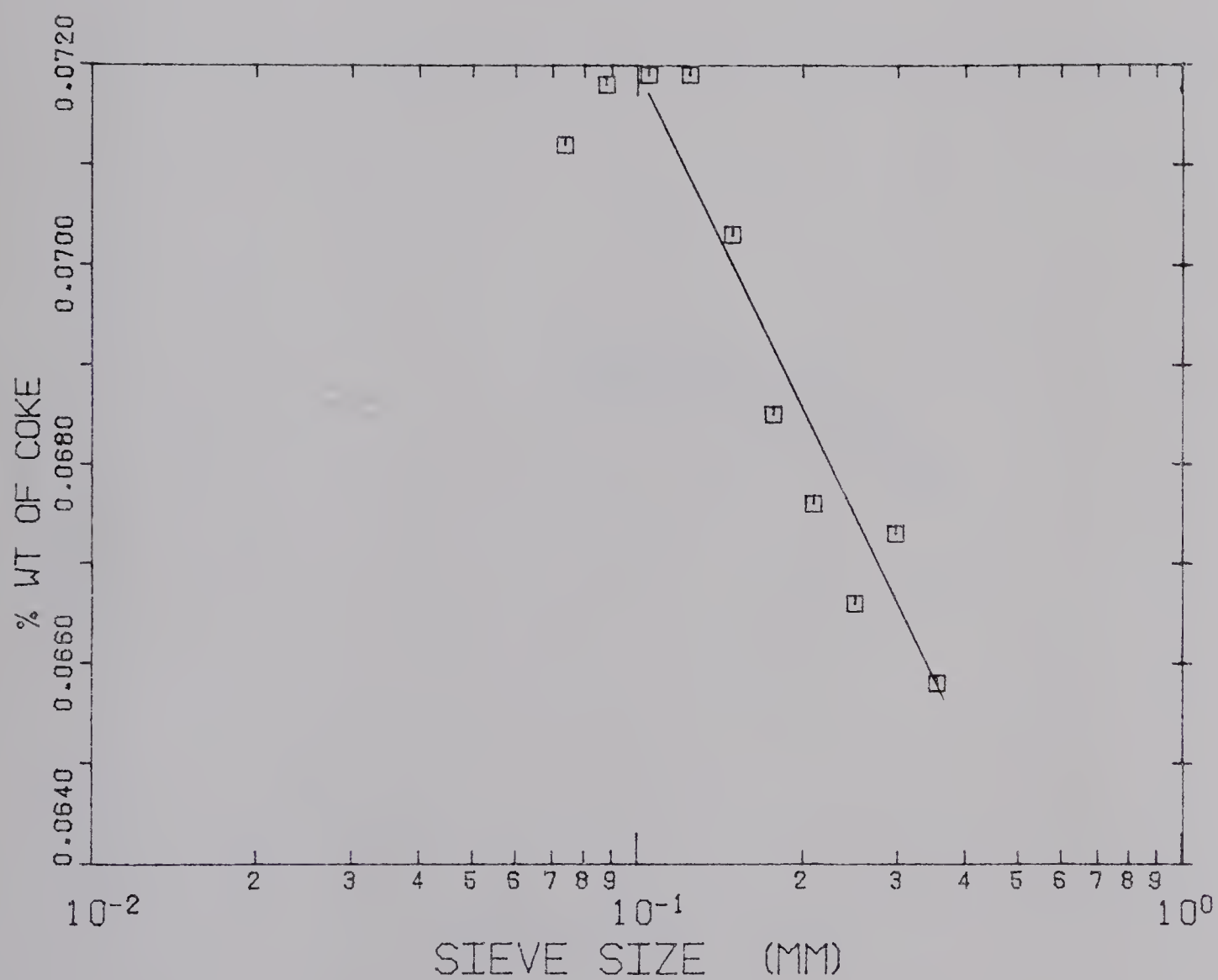


Figure 33. Nickel Content in Fluid Coke as a Function of Particle Size, Dec 7, '78.

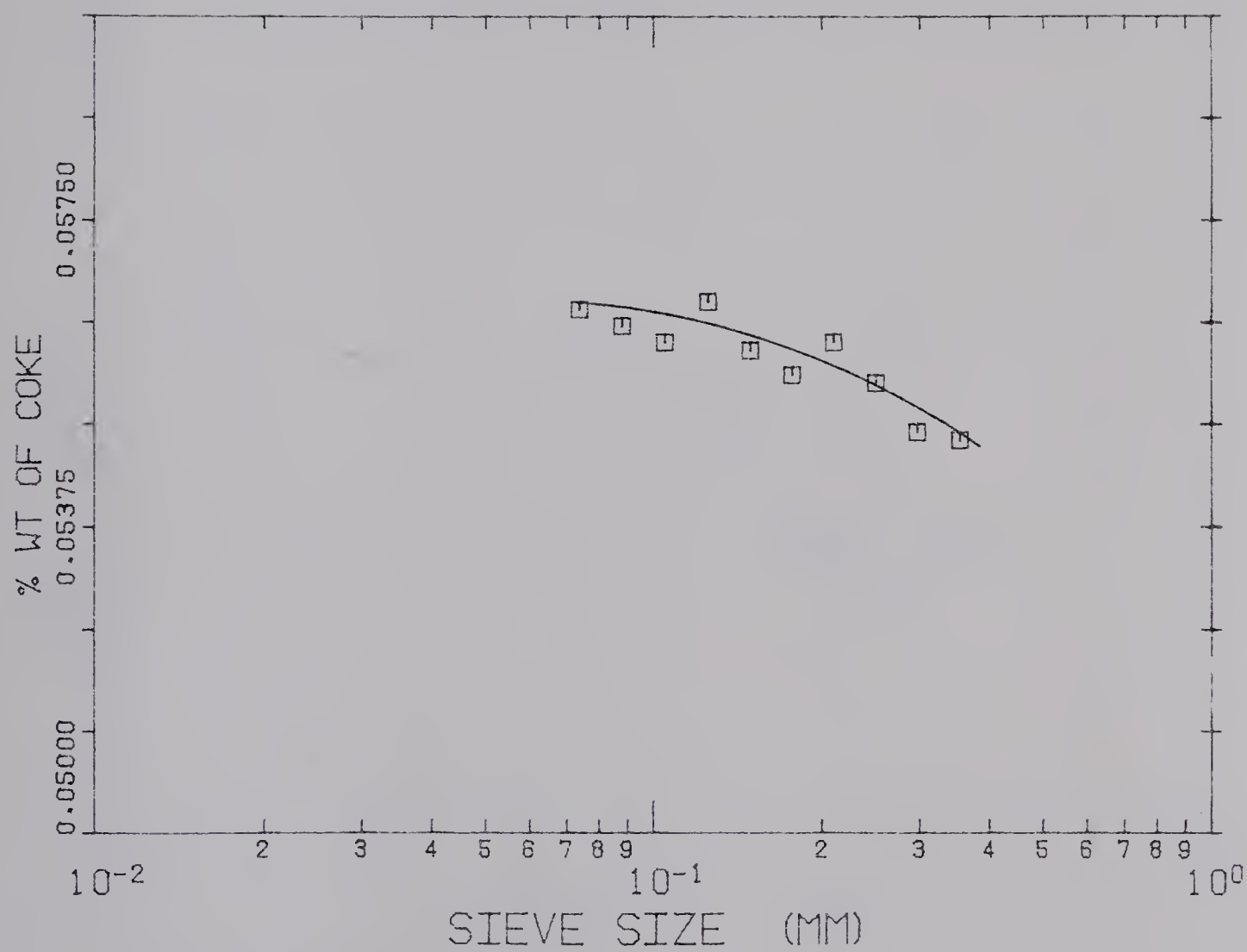


Figure 34. Nickel Content in Fluid Coke as a Function of Particle Size, Aug 12, '80.

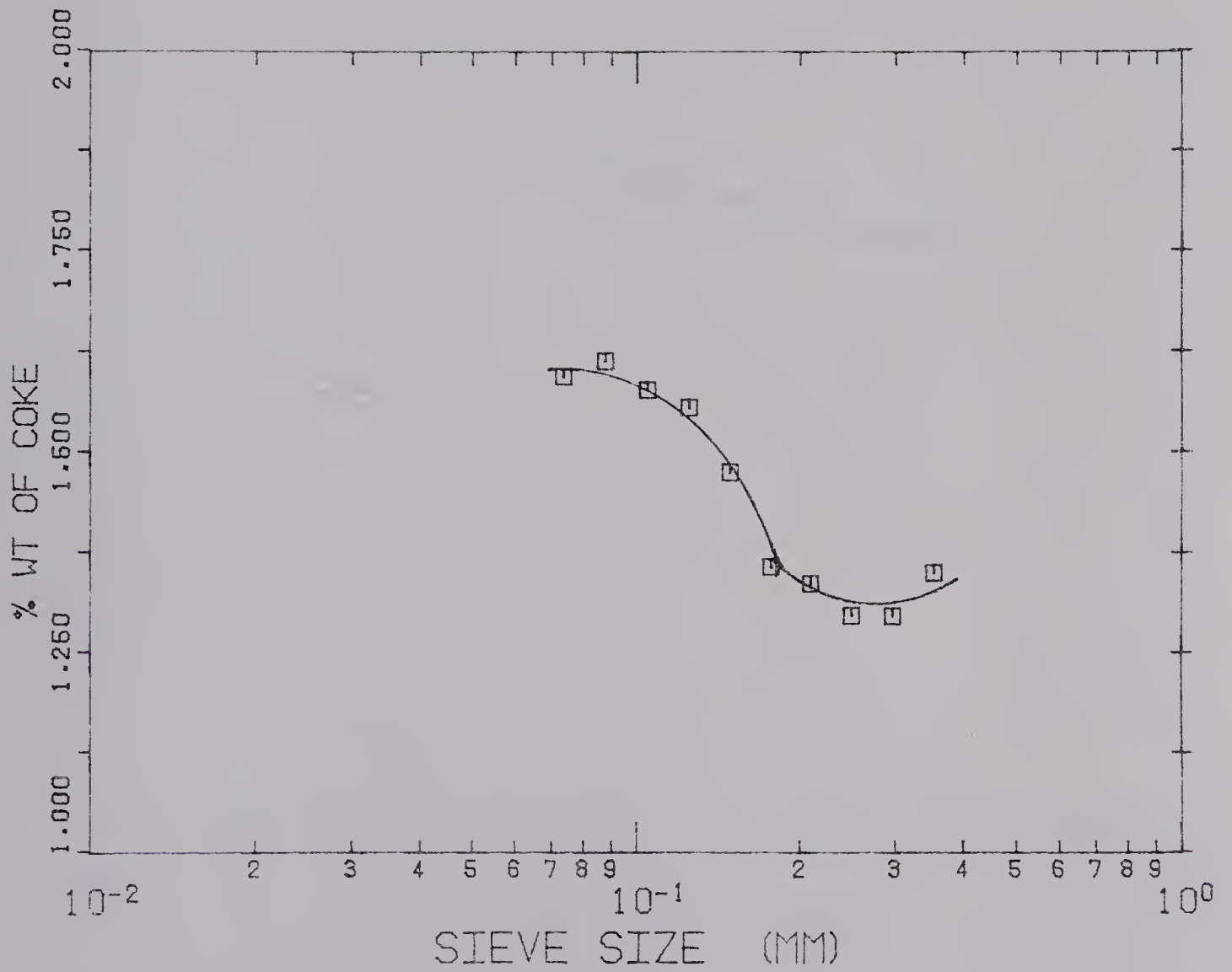


Figure 35. Silicon Content in Fluid Coke as a Function of Particle Size, Dec 7, '78.

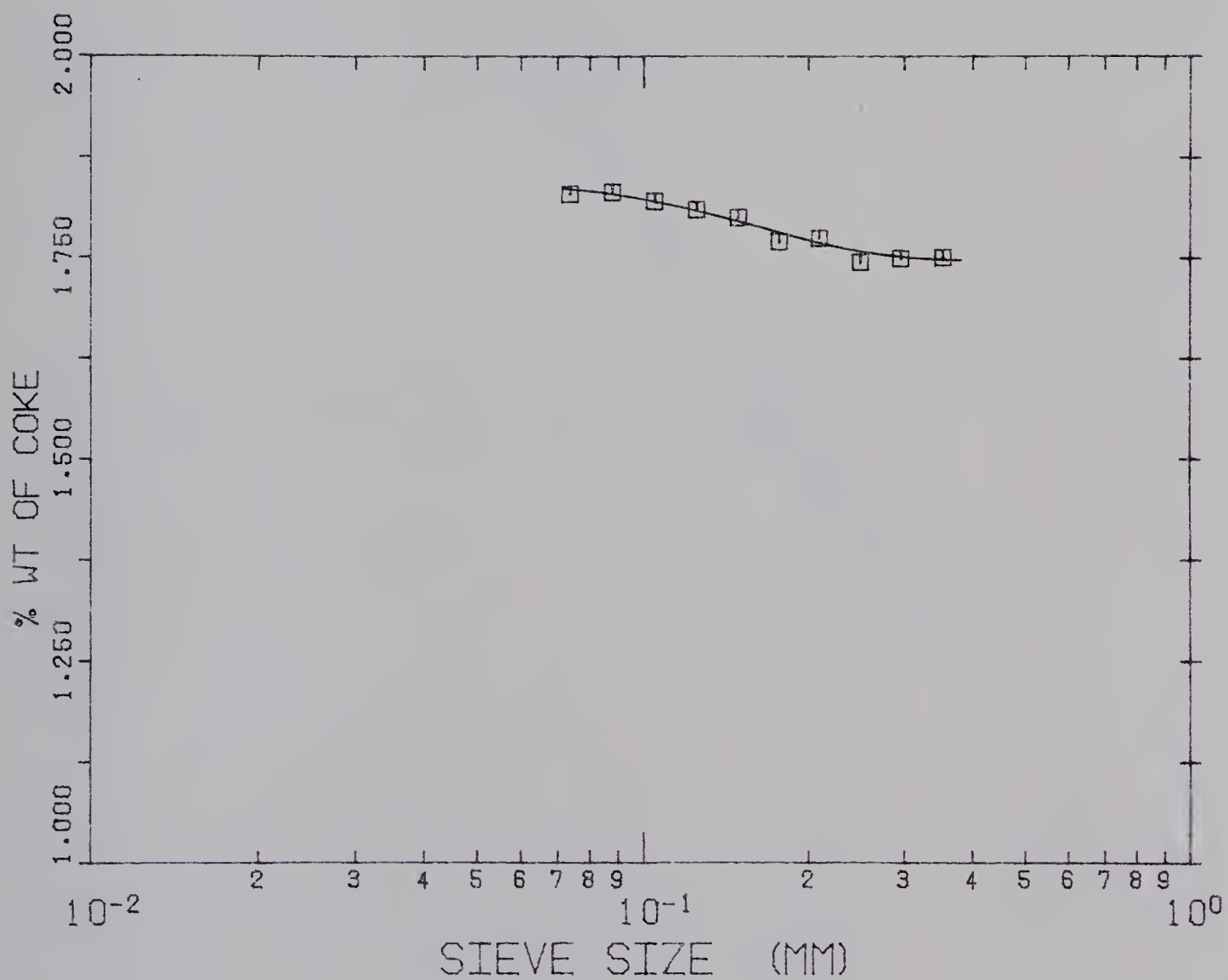


Figure 36. Silicon Content in Fluid Coke as a Function of Particle Size, Aug 12, '80.

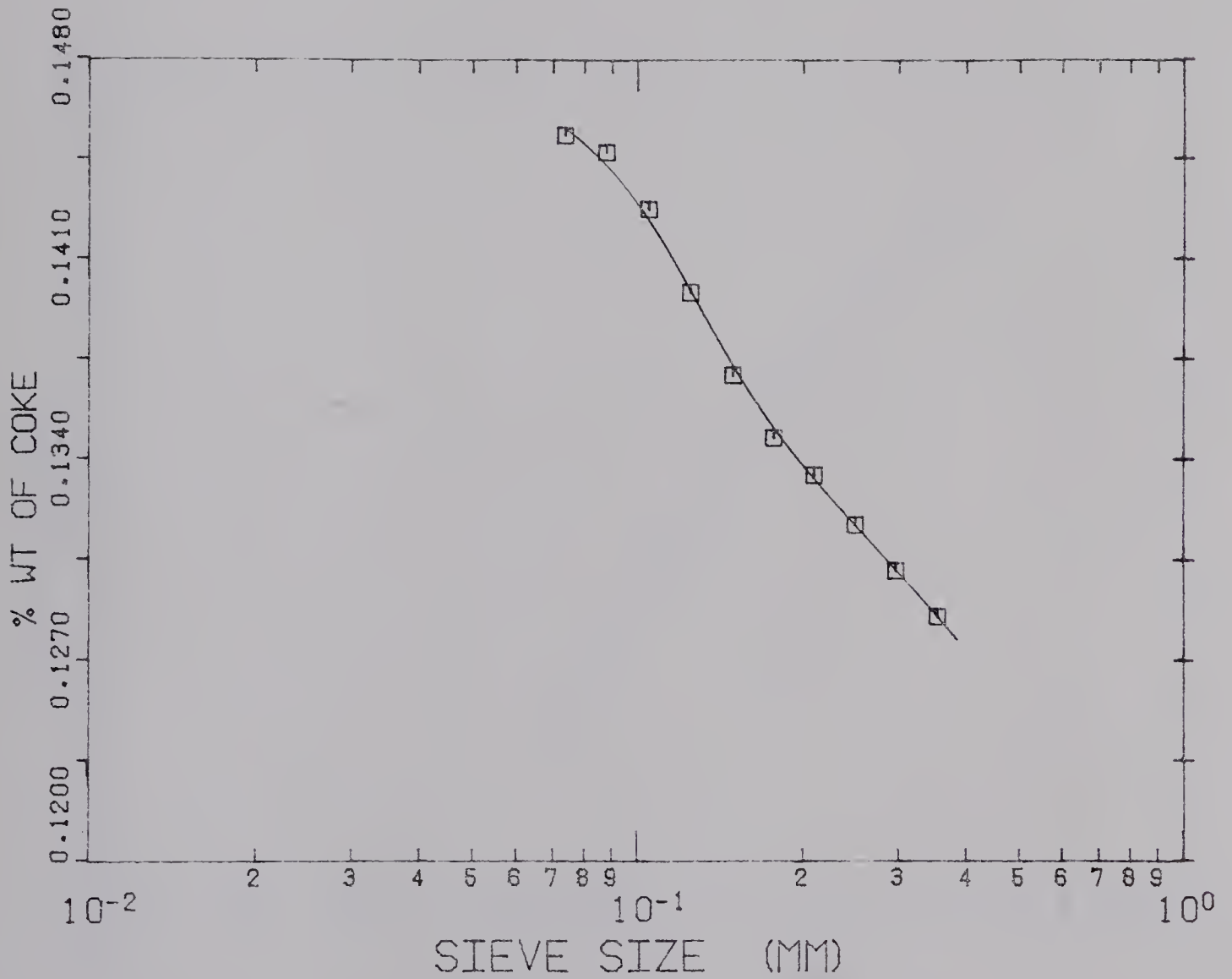


Figure 37. Titanium Content in Fluid Coke as a Function of Particle Size, Dec 7, '78.

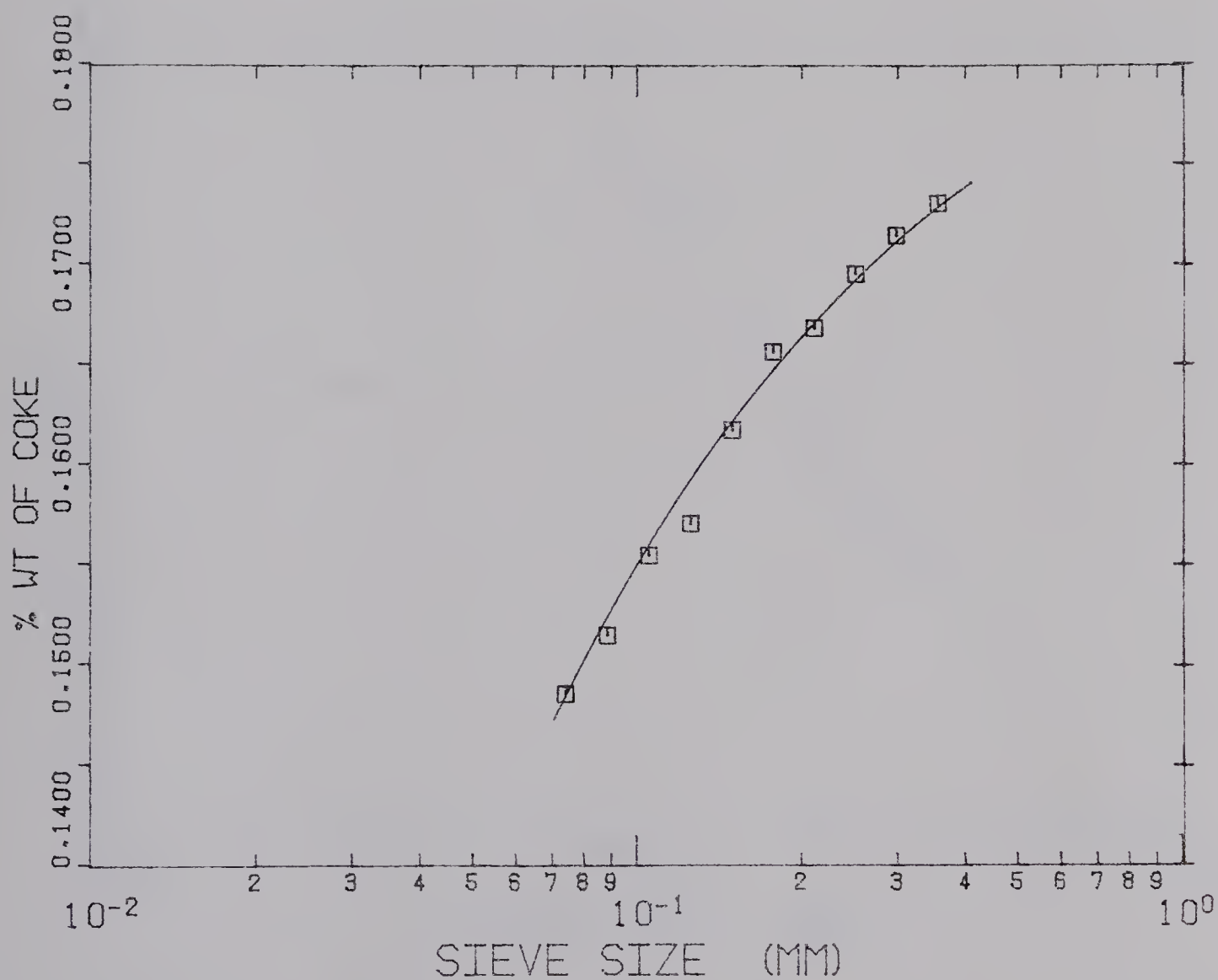


Figure 38. Titanium Content in Fluid Coke as a Function of Particle Size, Aug 12, '80.

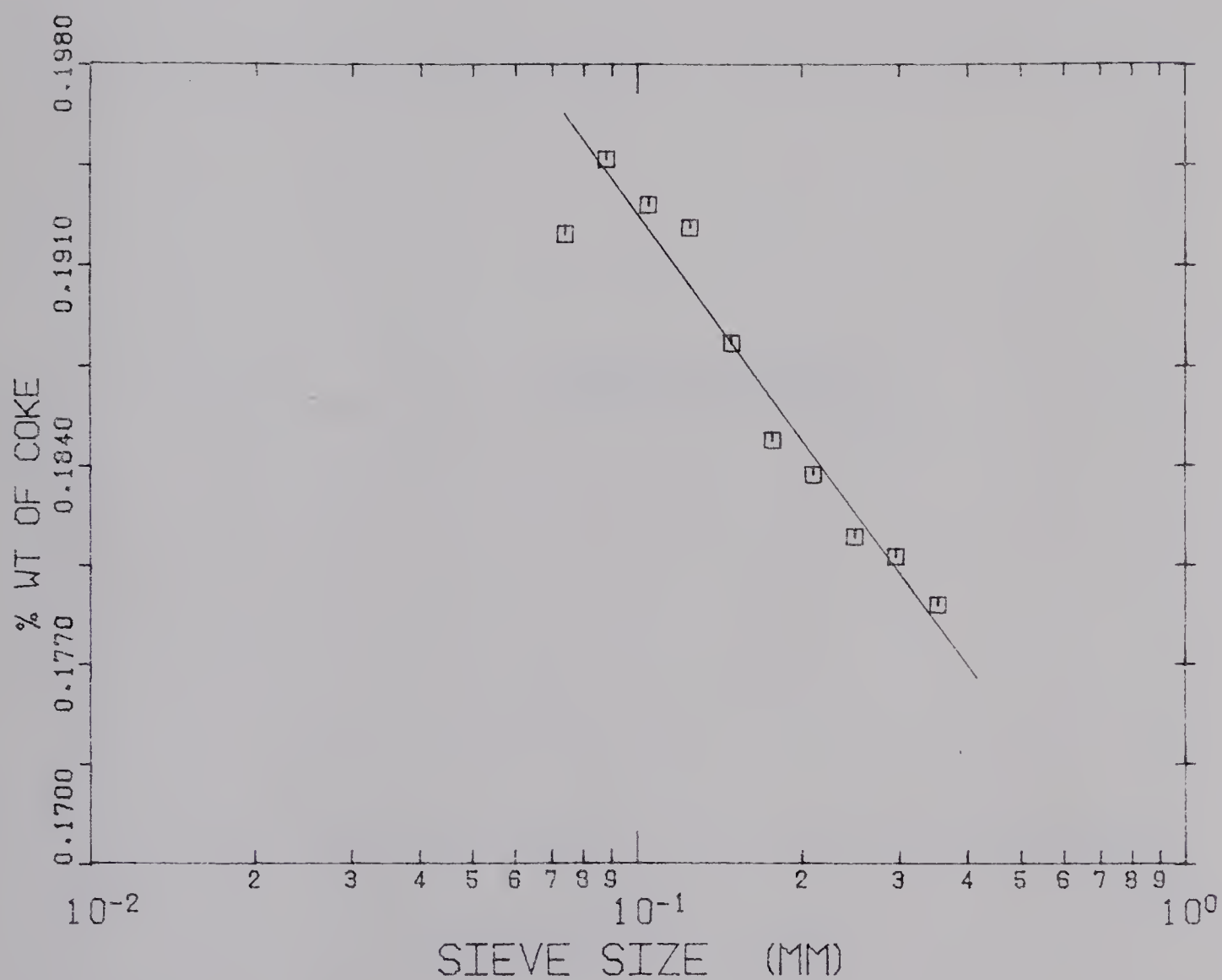


Figure 39. Vanadium Content in Fluid Coke as a Function of Particle Size, Dec 7, '78.

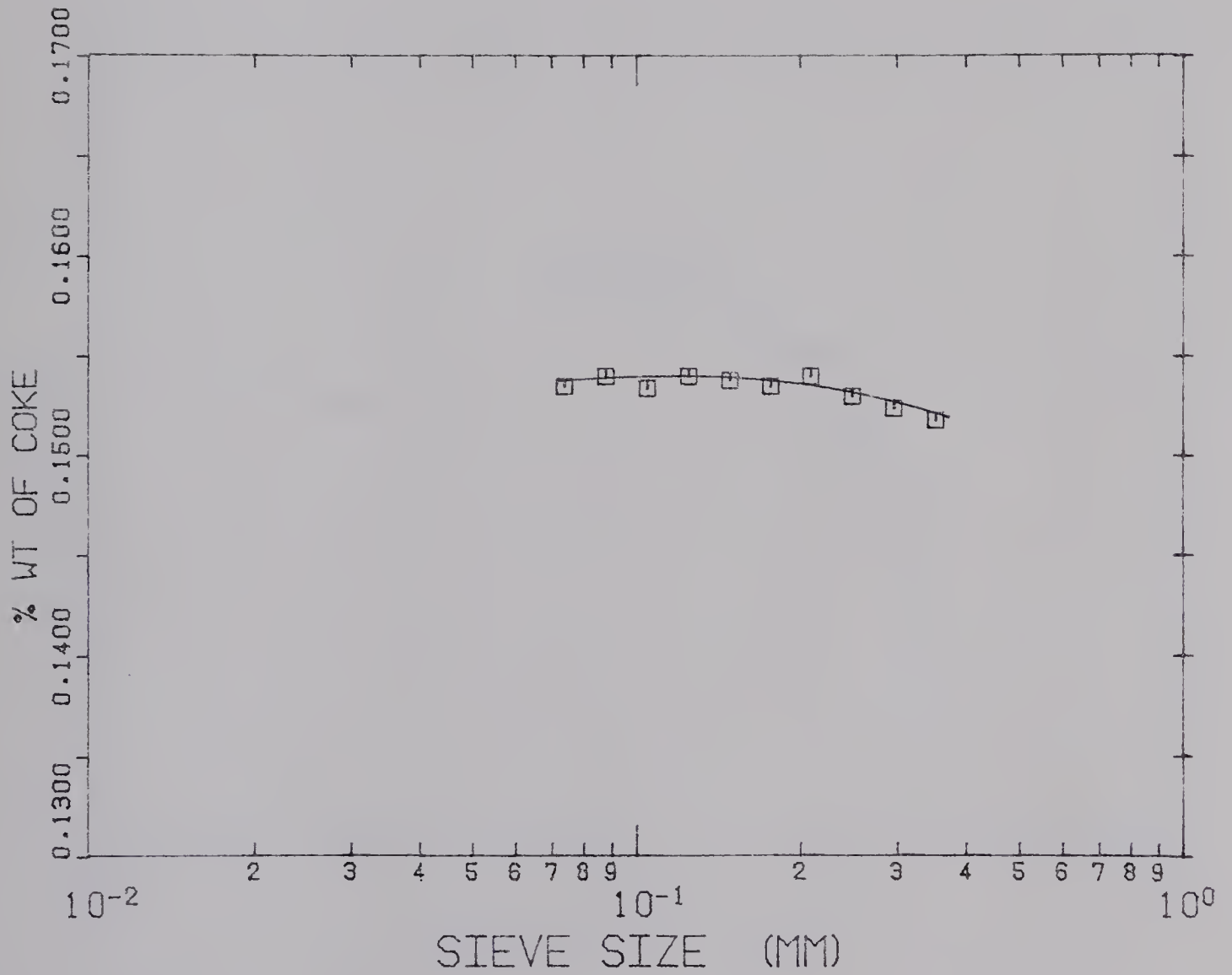


Figure 40. Vanadium Content in Fluid Coke as a Function of Particle Size, Aug 12, '80.

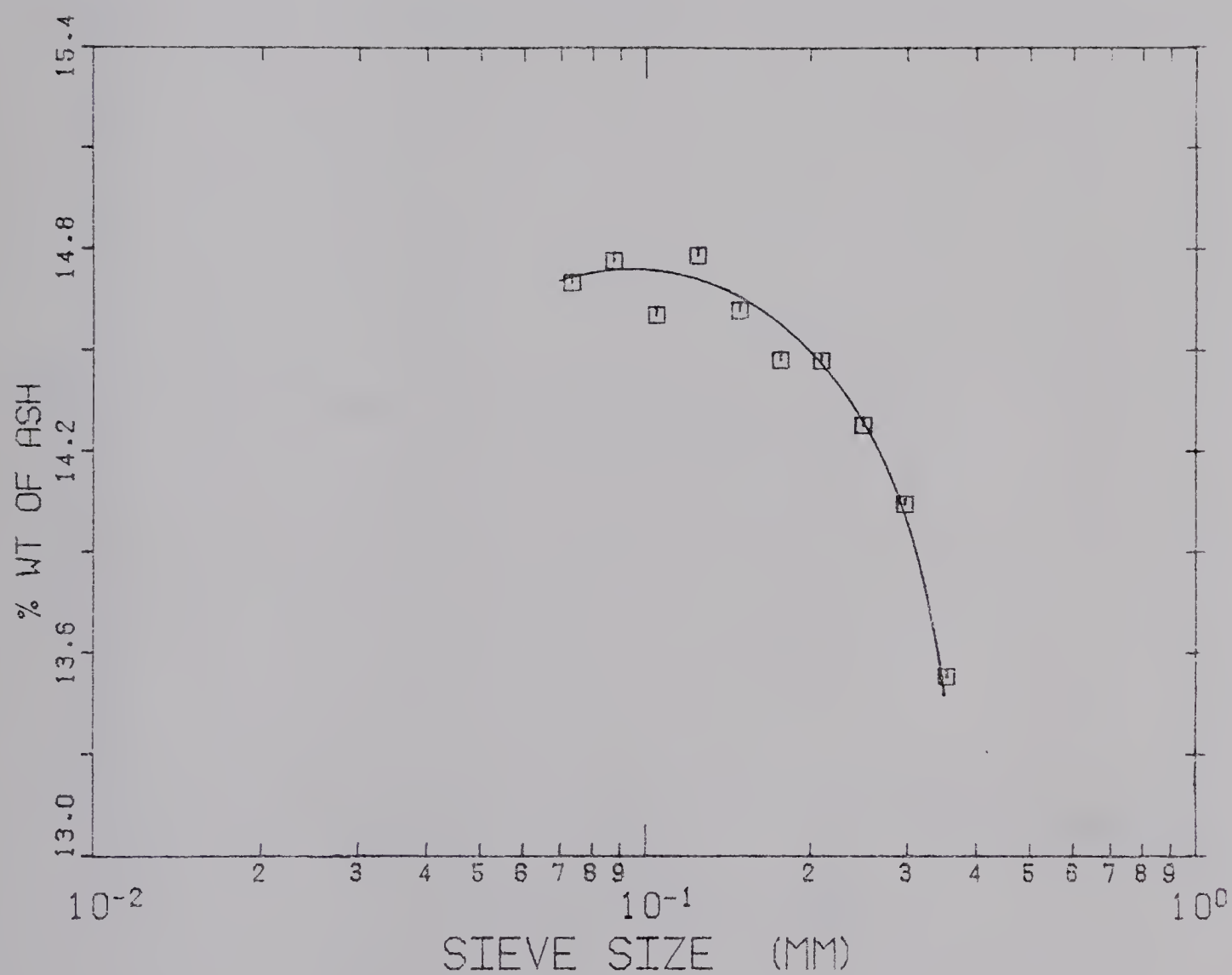


Figure 41. Aluminum Content in Fluid Coke Ash as a Function of Particle Size, Dec 7, '78.

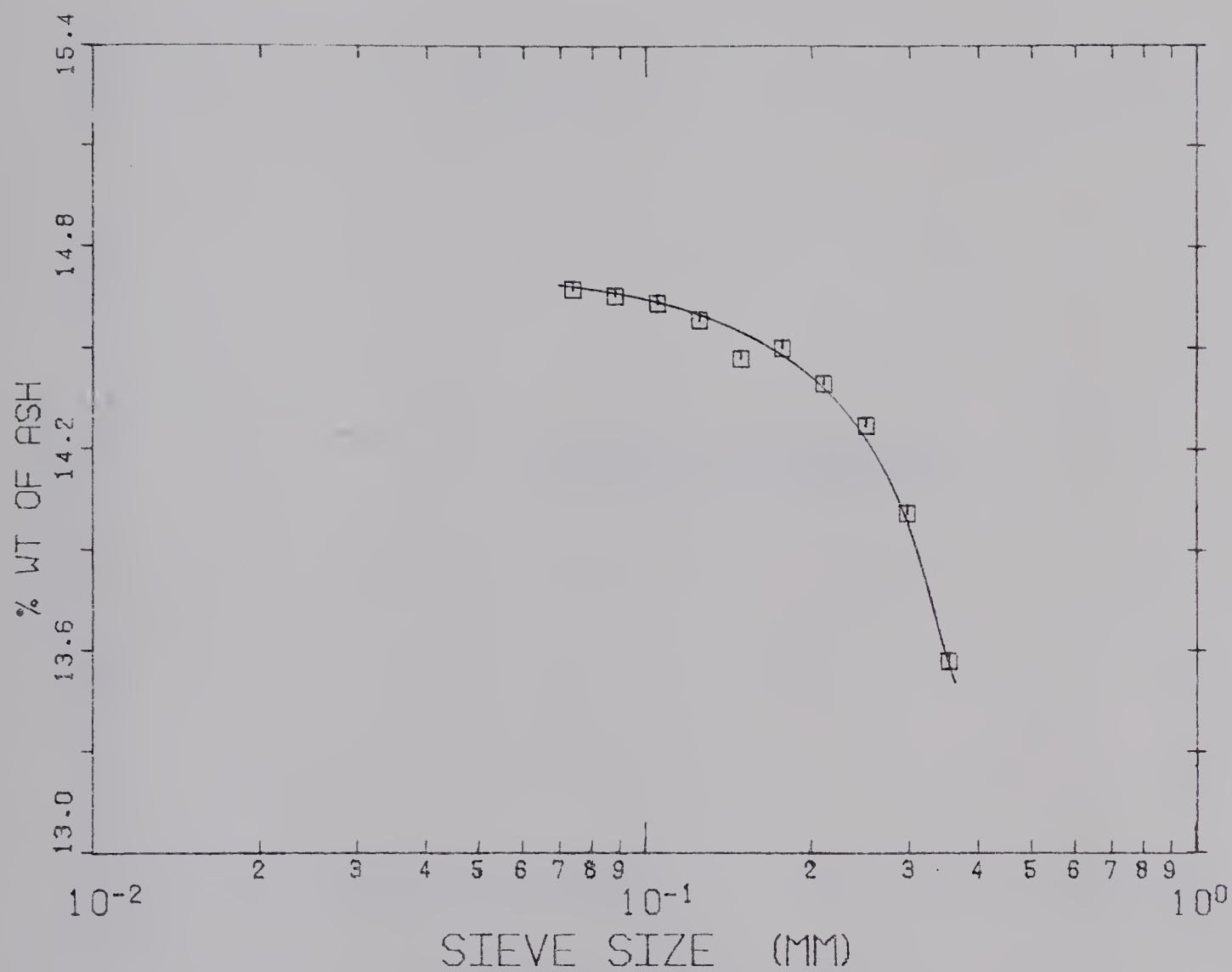


Figure 42. Aluminum Content in Fluid Coke Ash as a Function of Particle Size, Aug 12, '80.

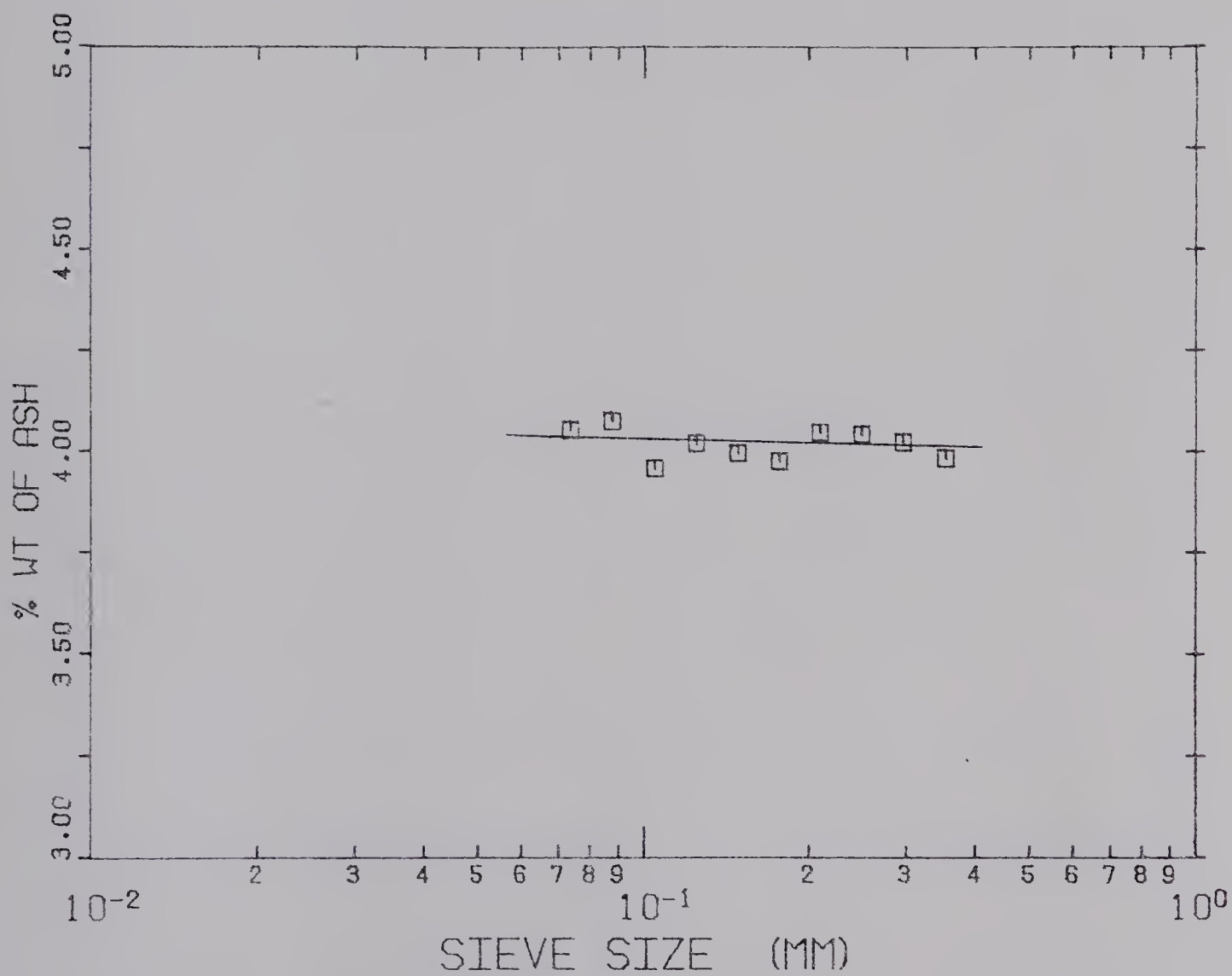


Figure 43. Calcium Content in Fluid Coke Ash as a Function of Particle Size, Dec 7, '78.

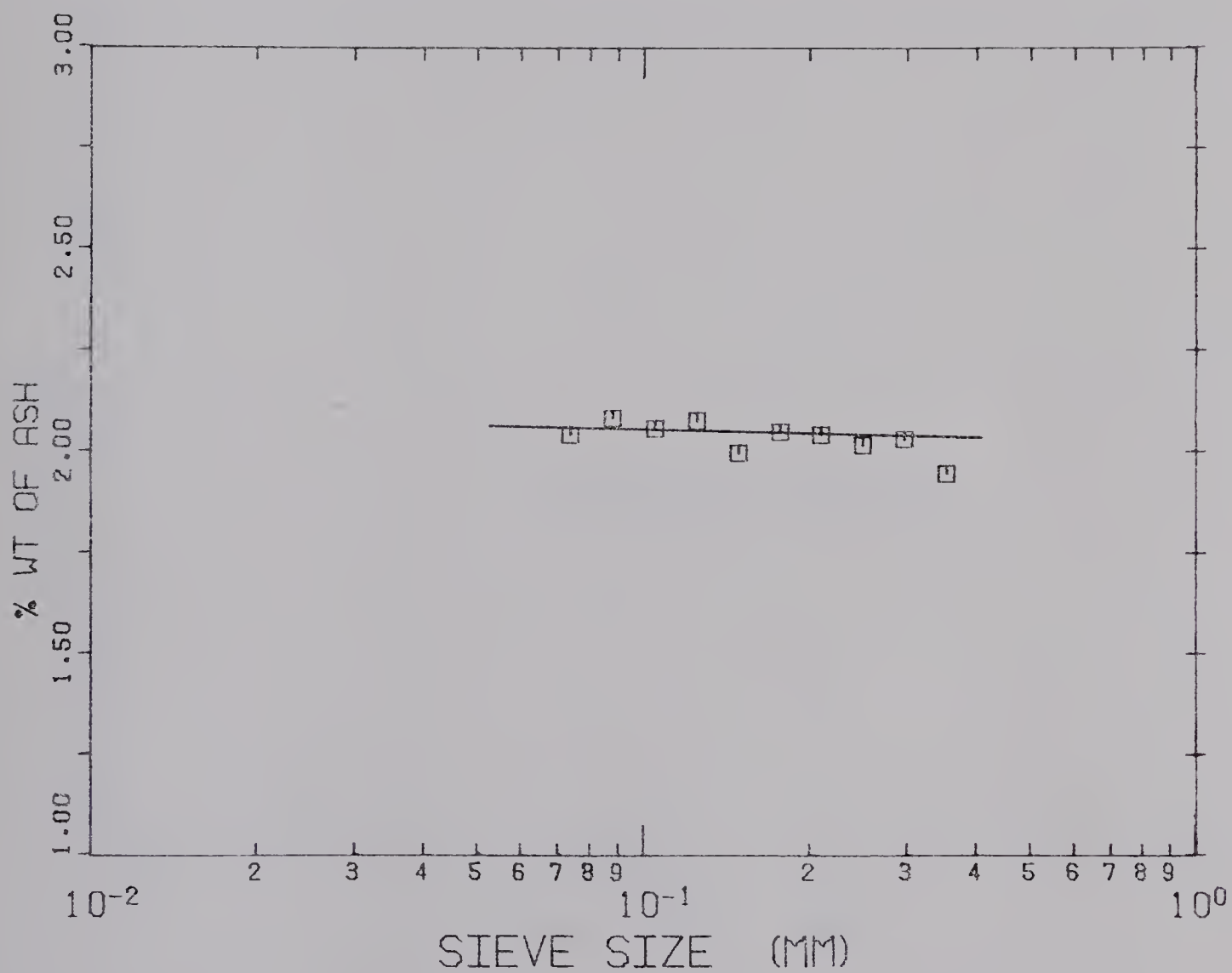


Figure 44. Calcium Content in Fluid Coke Ash as a Function of Particle Size, Aug 12, '80.

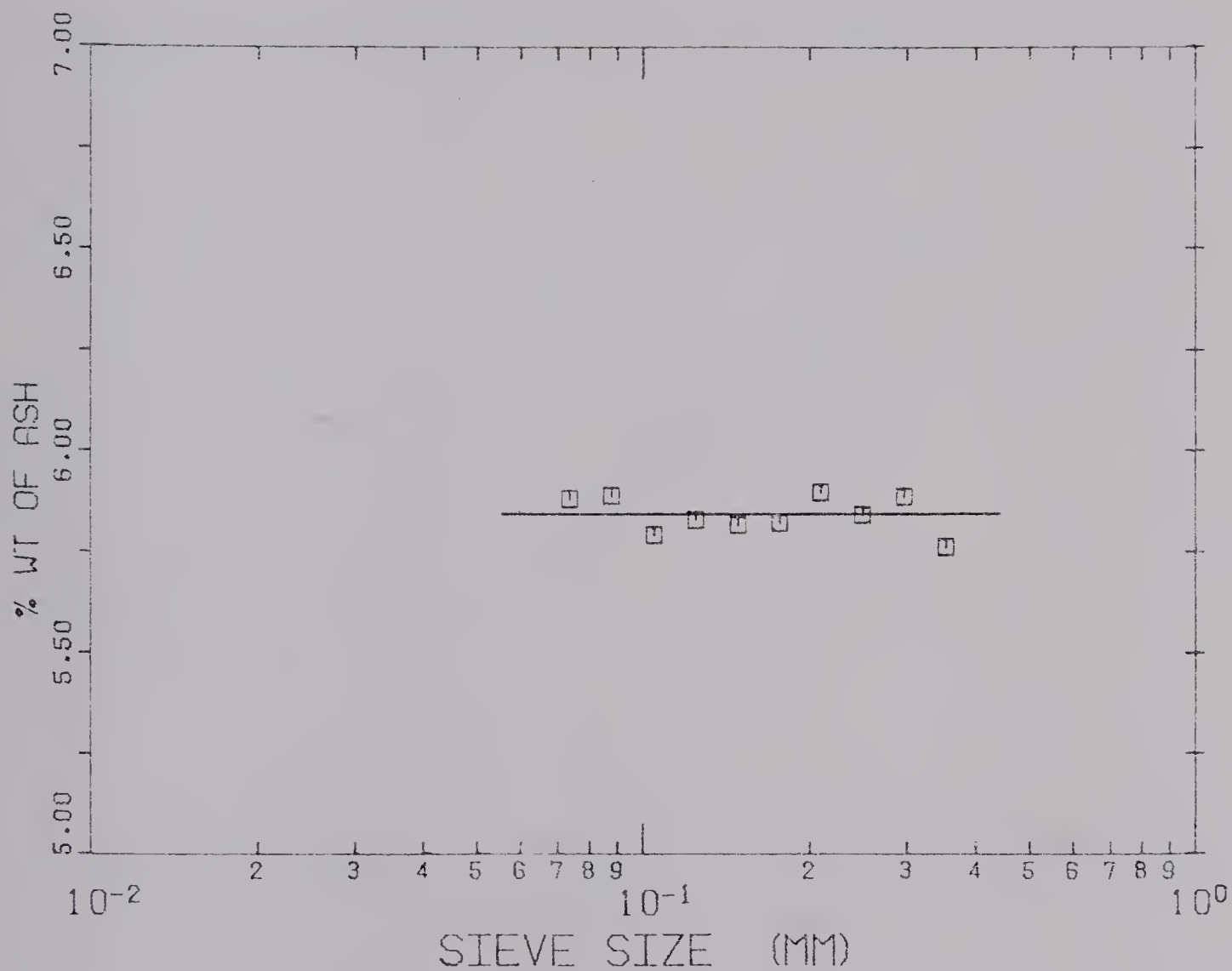


Figure 45. Iron Content in Fluid Coke Ash as a Function of Particle Size, Dec 7, '78.

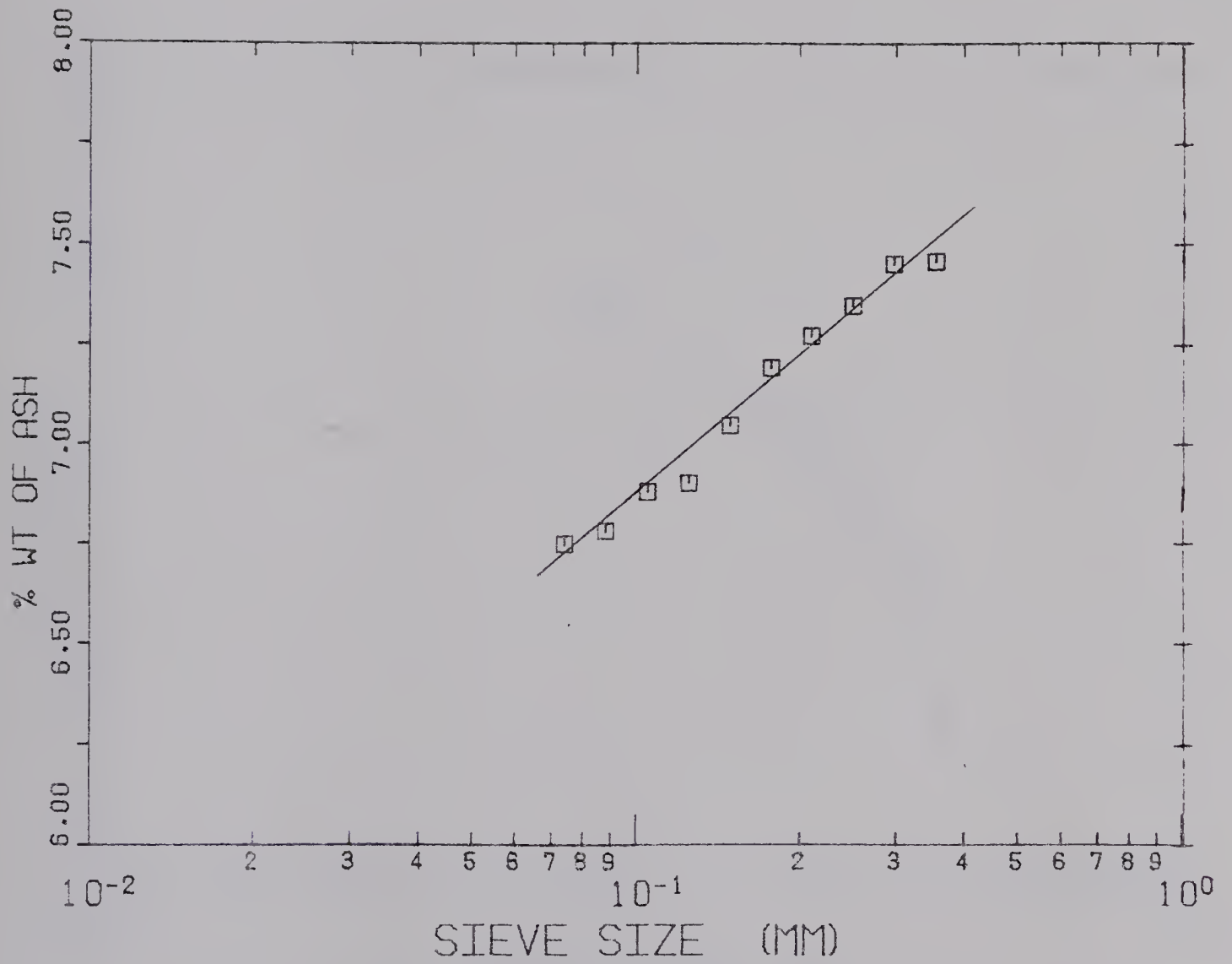


Figure 46. Iron Content in Fluid Coke Ash as a Function of Particle Size, Aug 12, '80.

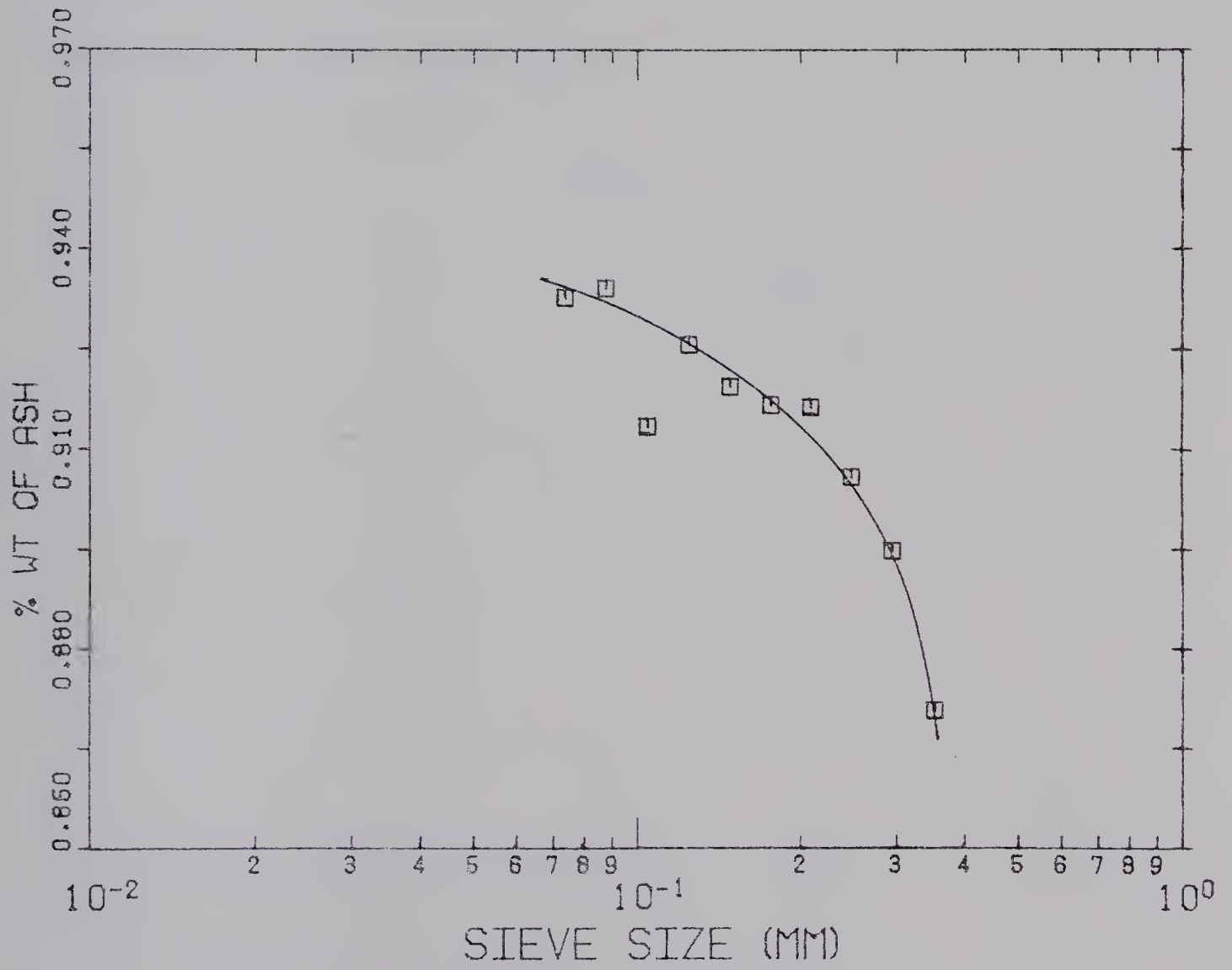


Figure 47. Magnesium Content in Fluid Coke Ash as a Function of Particle Size, Dec 7, '78.

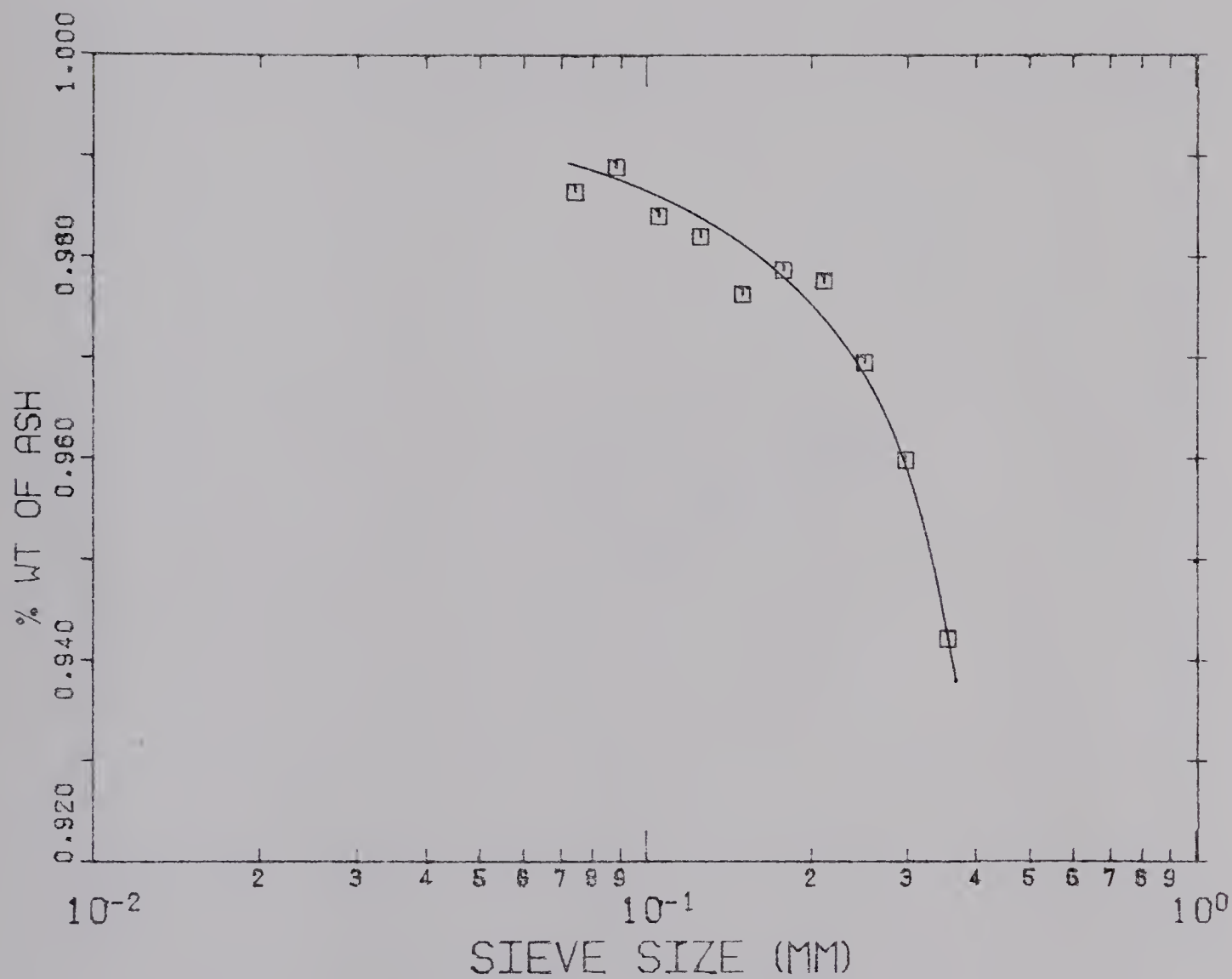


Figure 48. Magnesium Content in Fluid Coke Ash as a Function of Particle Size, Aug 12, '80.

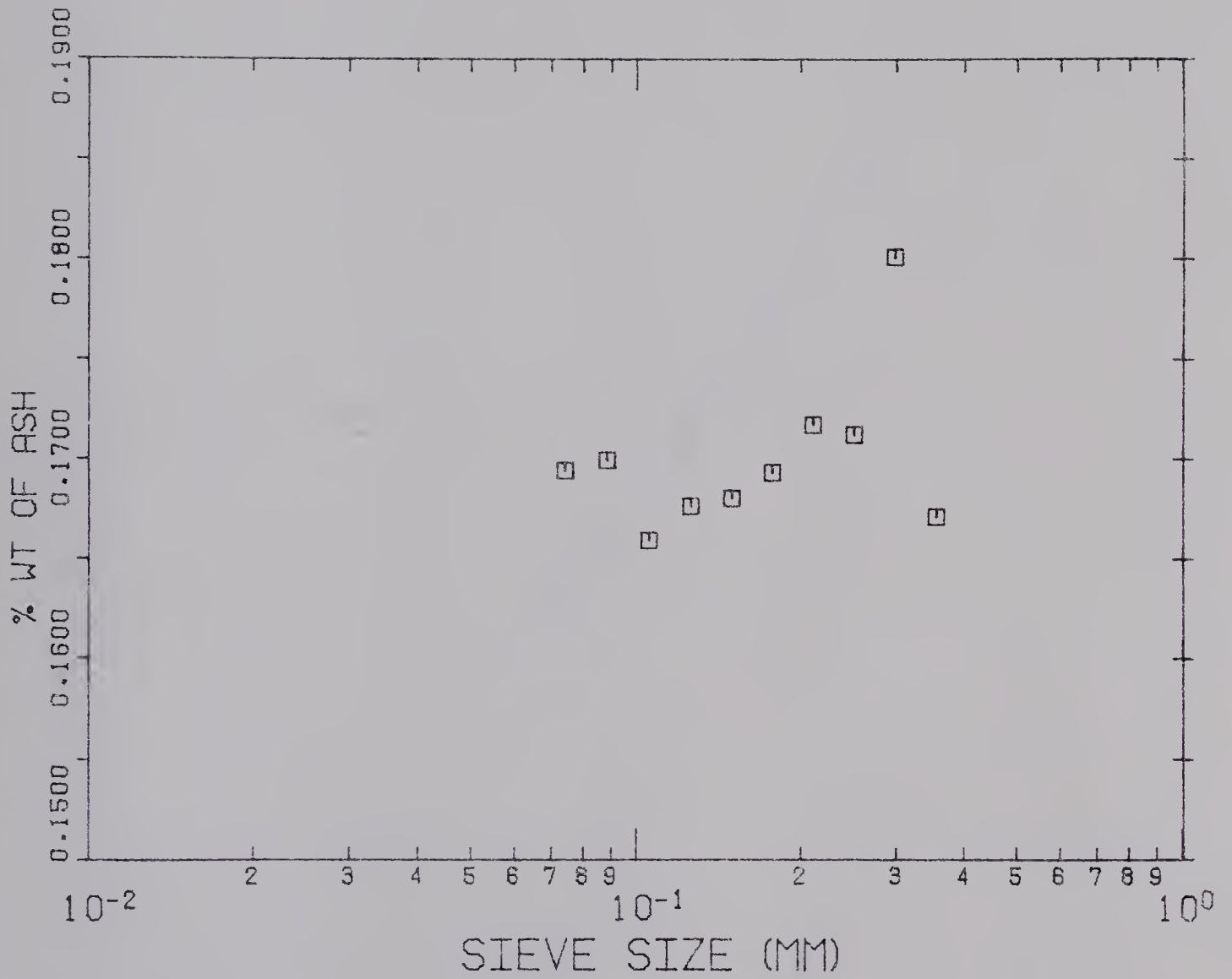


Figure 49. Manganese Content in Fluid Coke Ash as a Function of Particle Size, Dec 7, '78.

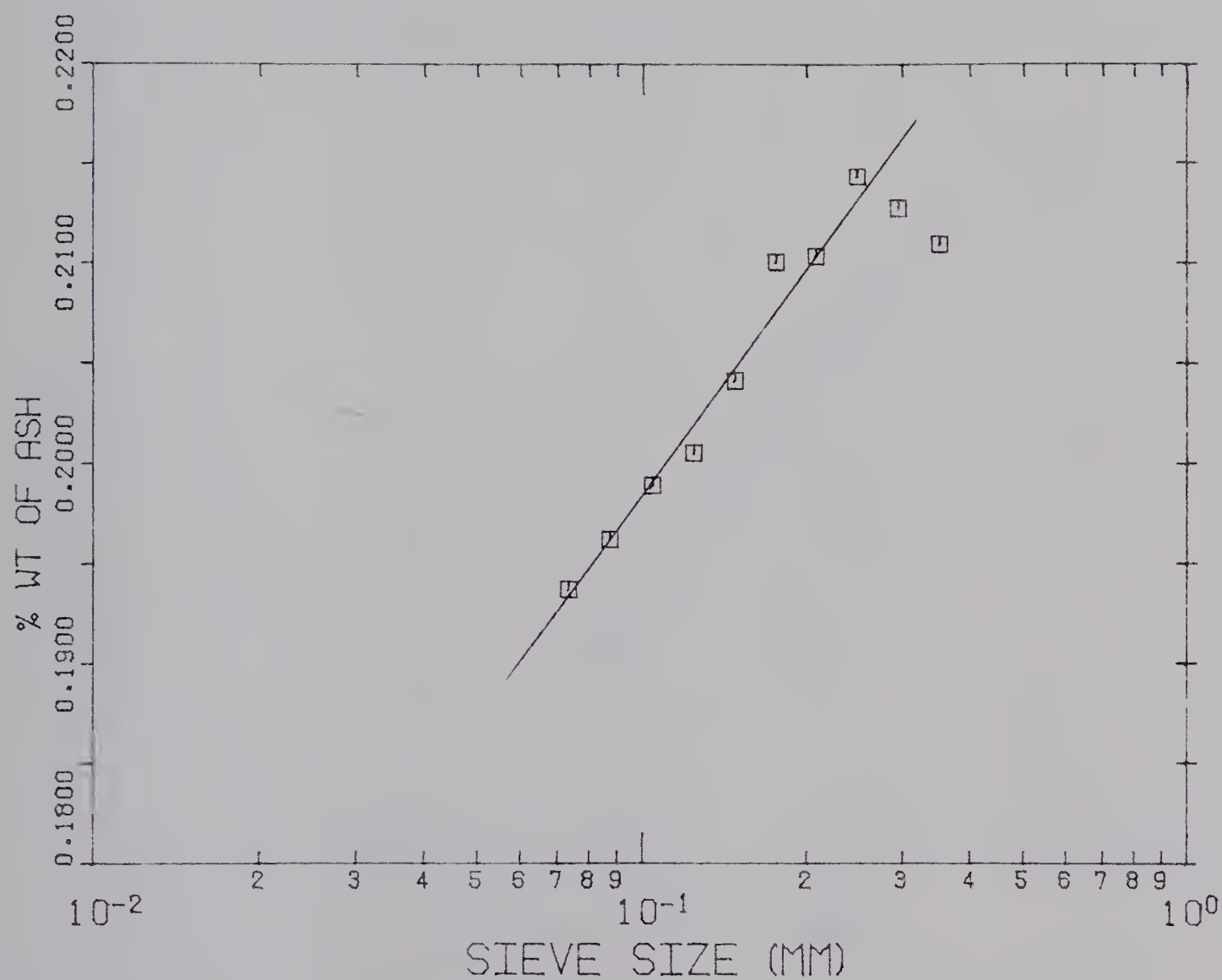


Figure 50. Manganese Content in Fluid Coke Ash as a Function of Particle Size, Aug 12, '80.

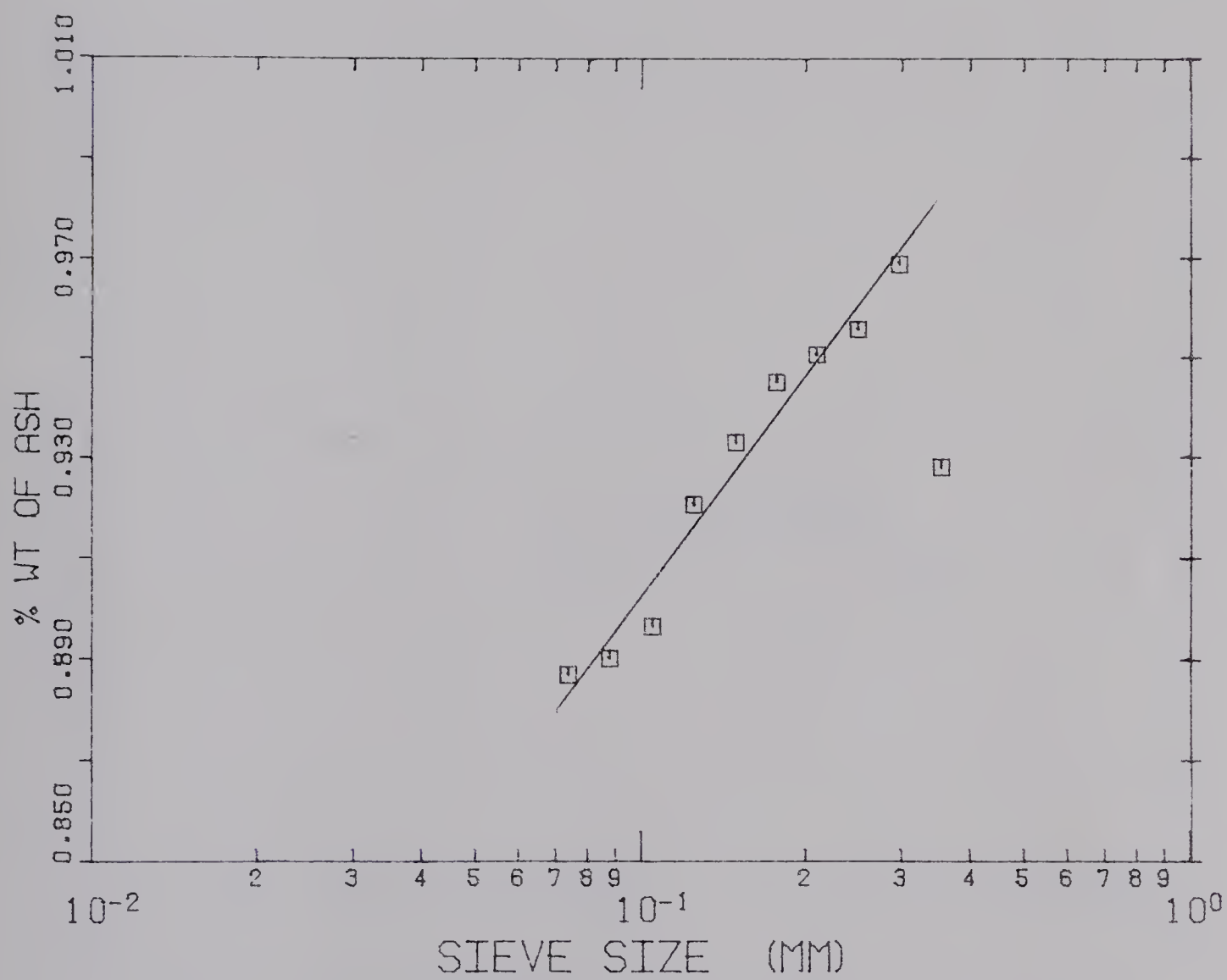


Figure 51. Nickel Content in Fluid Coke Ash as a Function of Particle Size, Dec 7, '78.

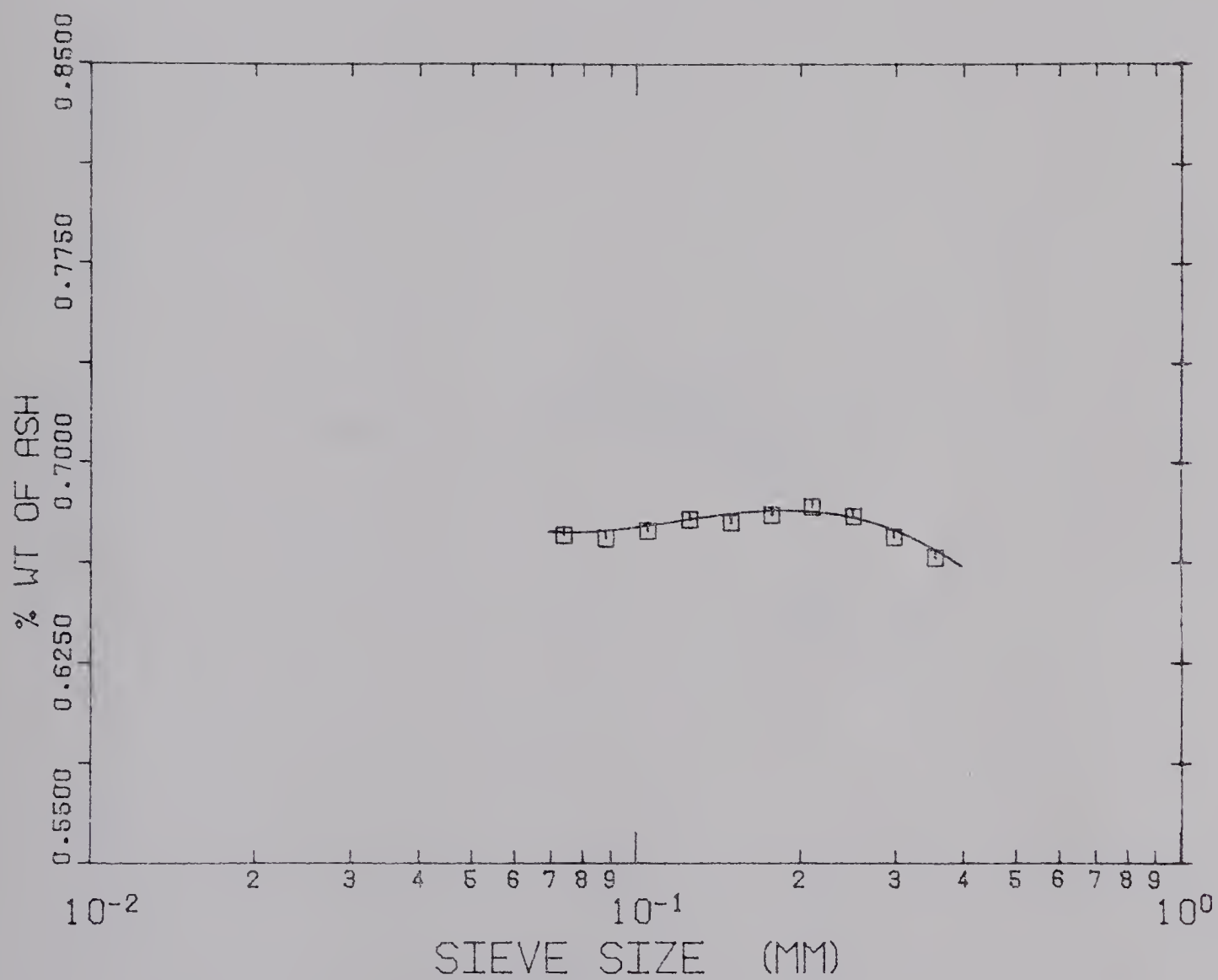


Figure 52. Nickel Content in Fluid Coke Ash as a Function of Particle Size, Aug 12, '80.

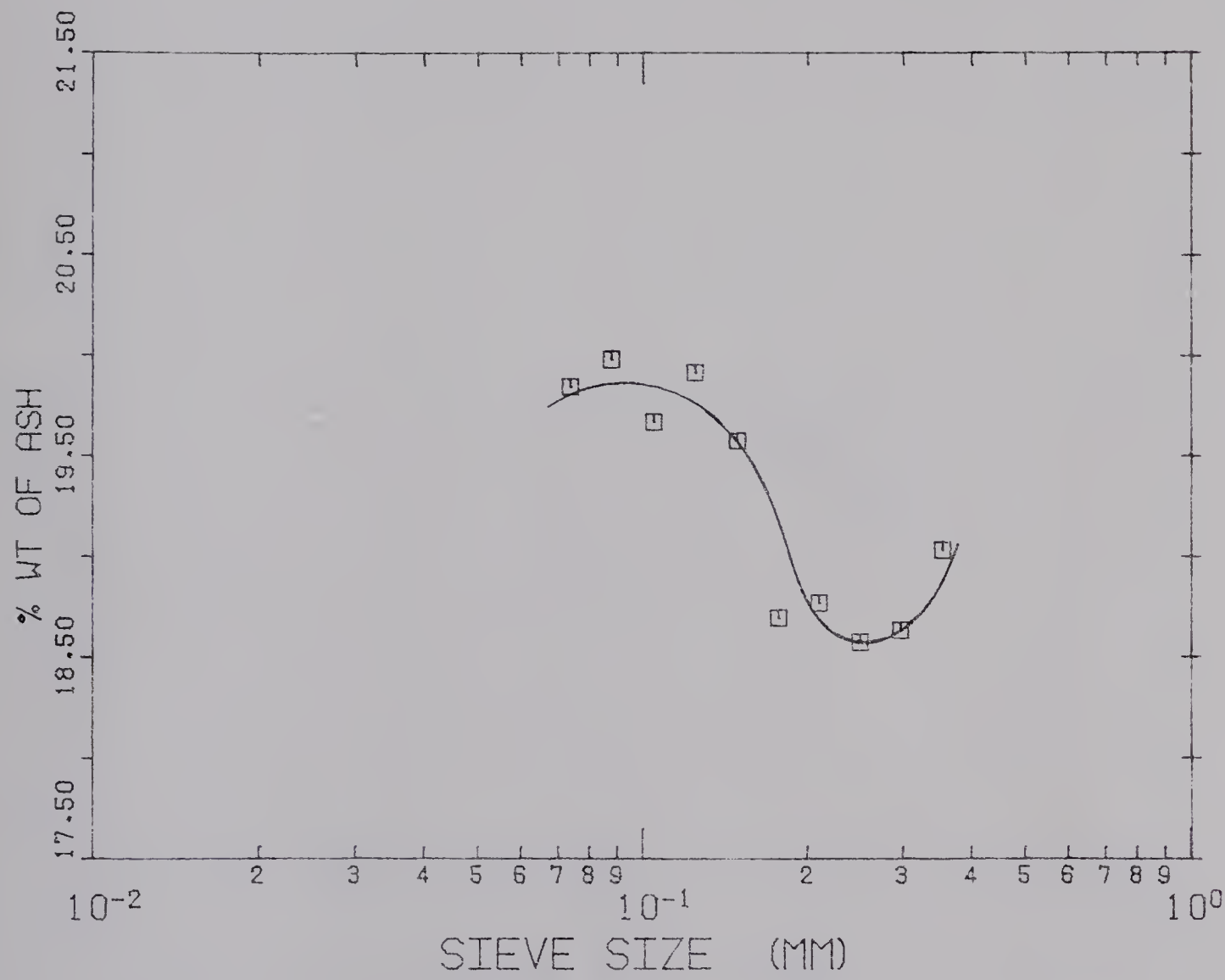


Figure 53. Silicon Content in Fluid Coke Ash as a Function of Particle Size, Dec 7, '78.

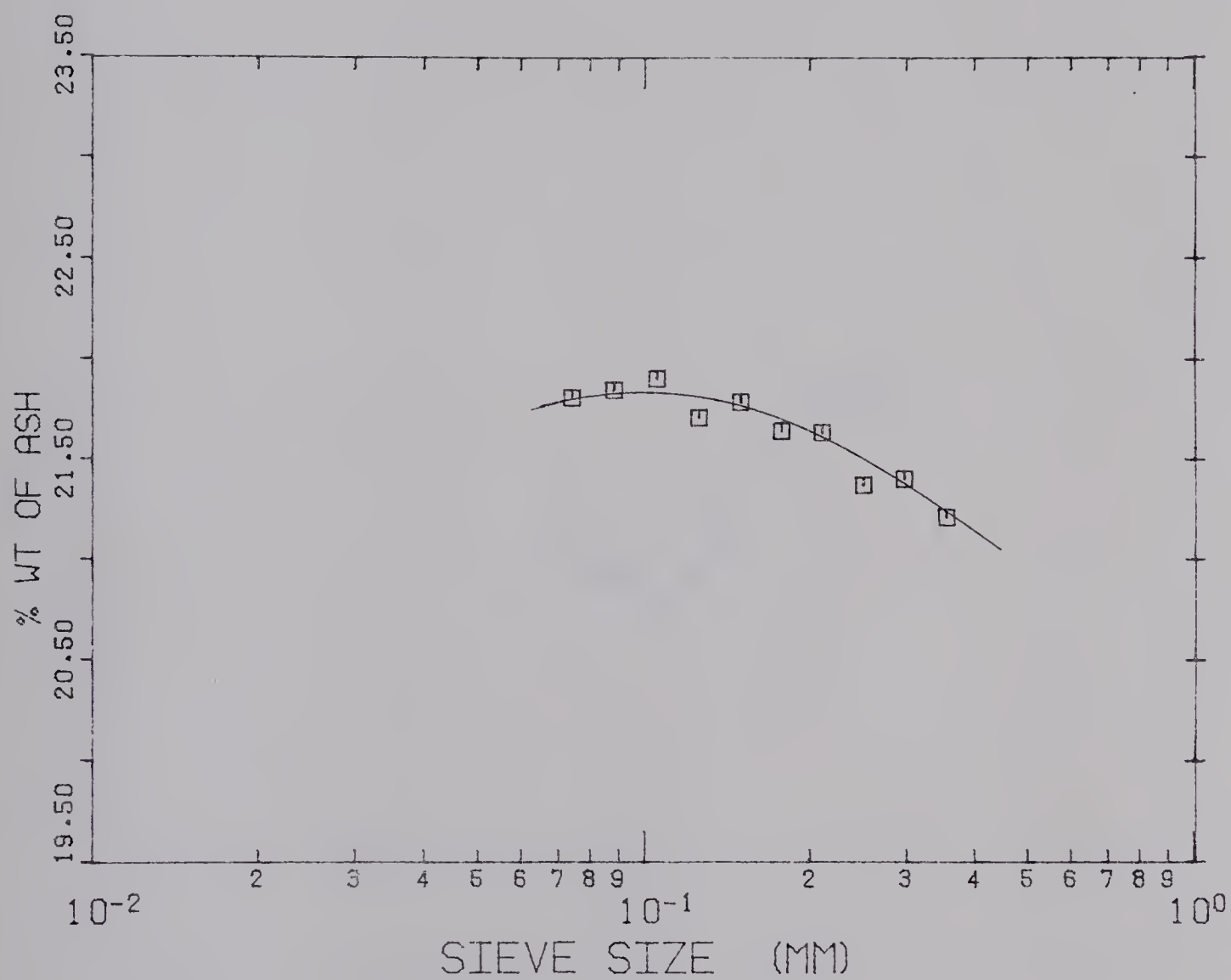


Figure 54. Silicon Content in Fluid Coke Ash as a Function of Particle Size, Aug 12, '80.

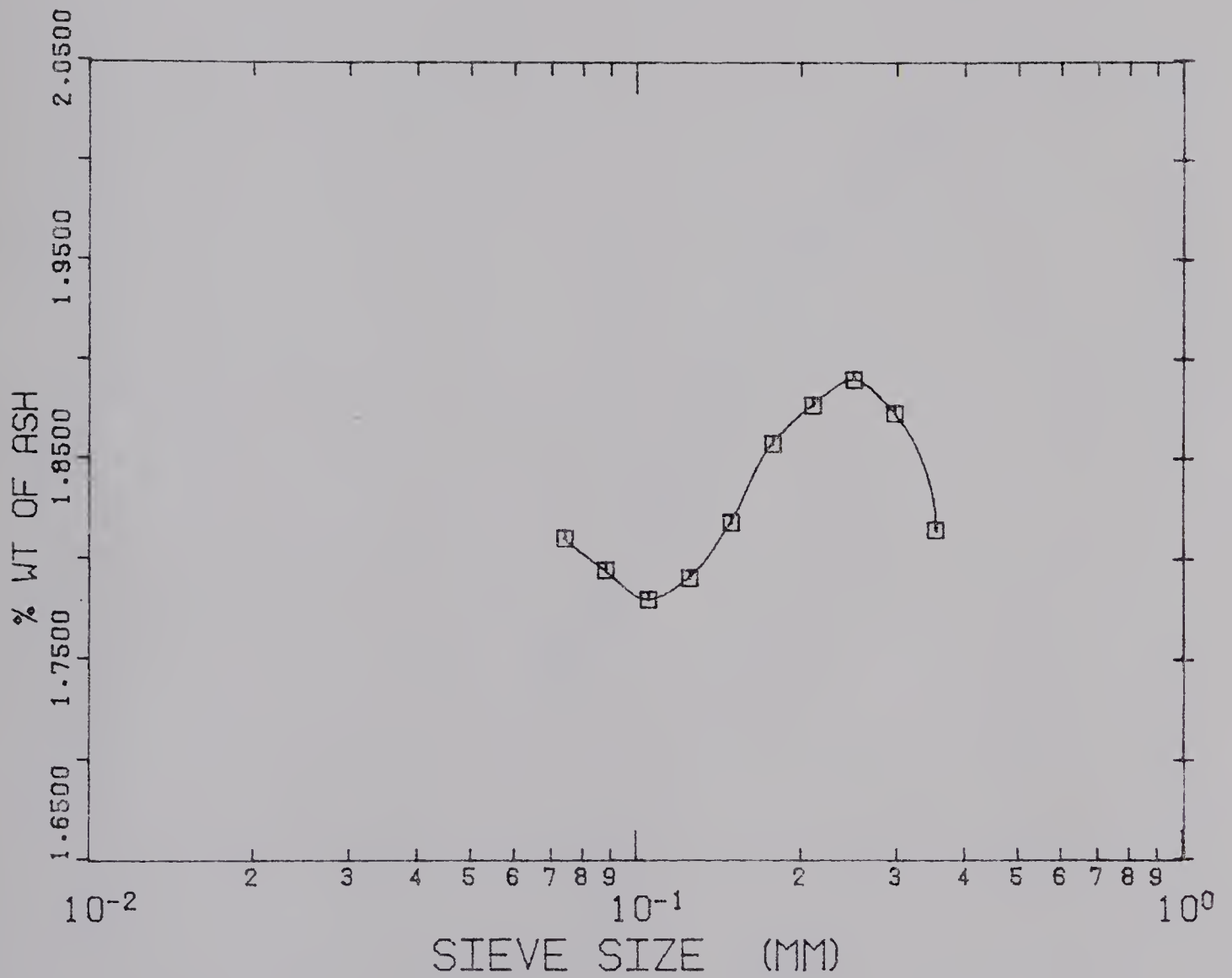


Figure 55. Titanium Content in Fluid Coke Ash as a Function of Particle Size, Dec 7, '78.

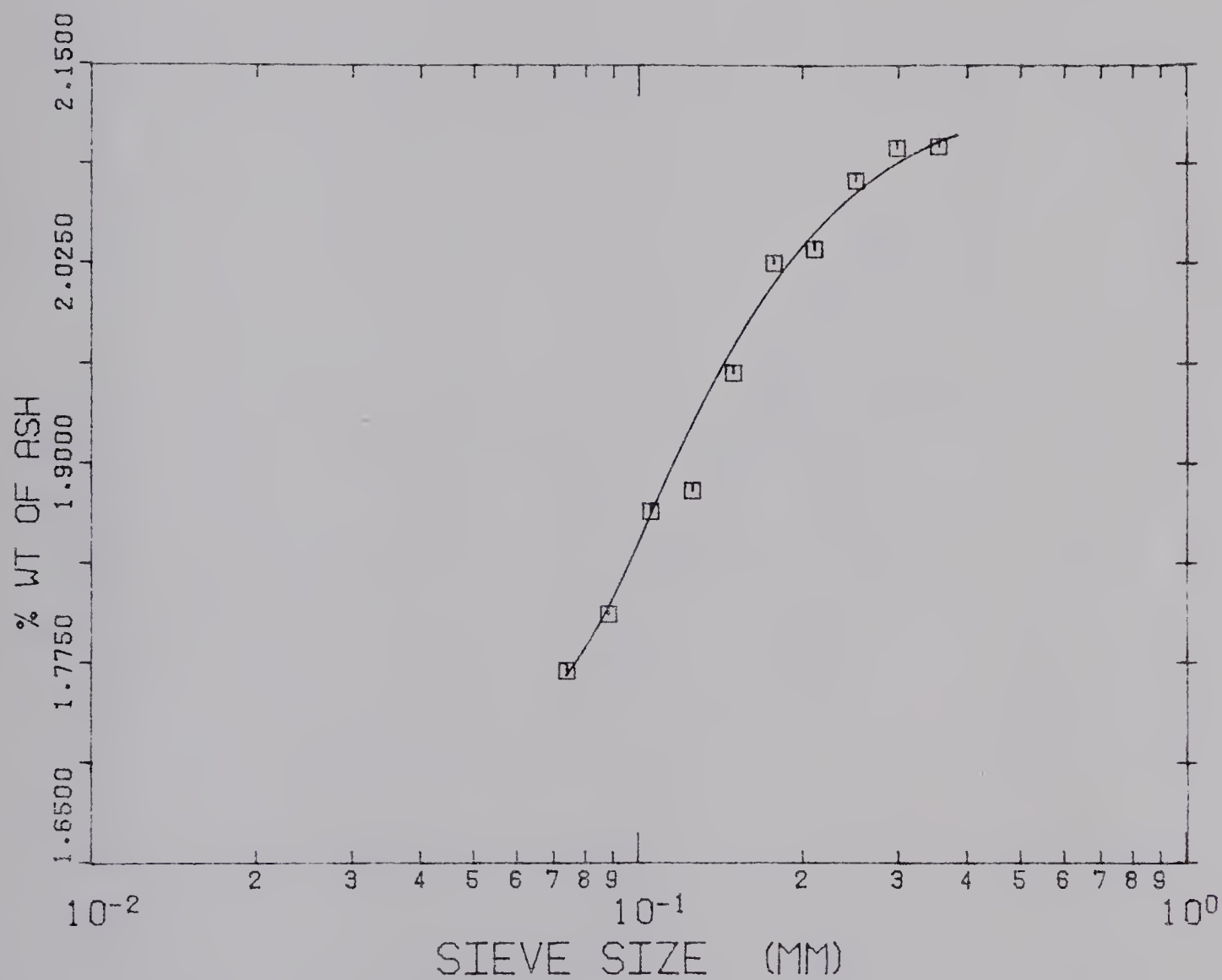


Figure 56. Titanium Content in Fluid Coke Ash as a Function of Particle Size, Aug 12, '80.

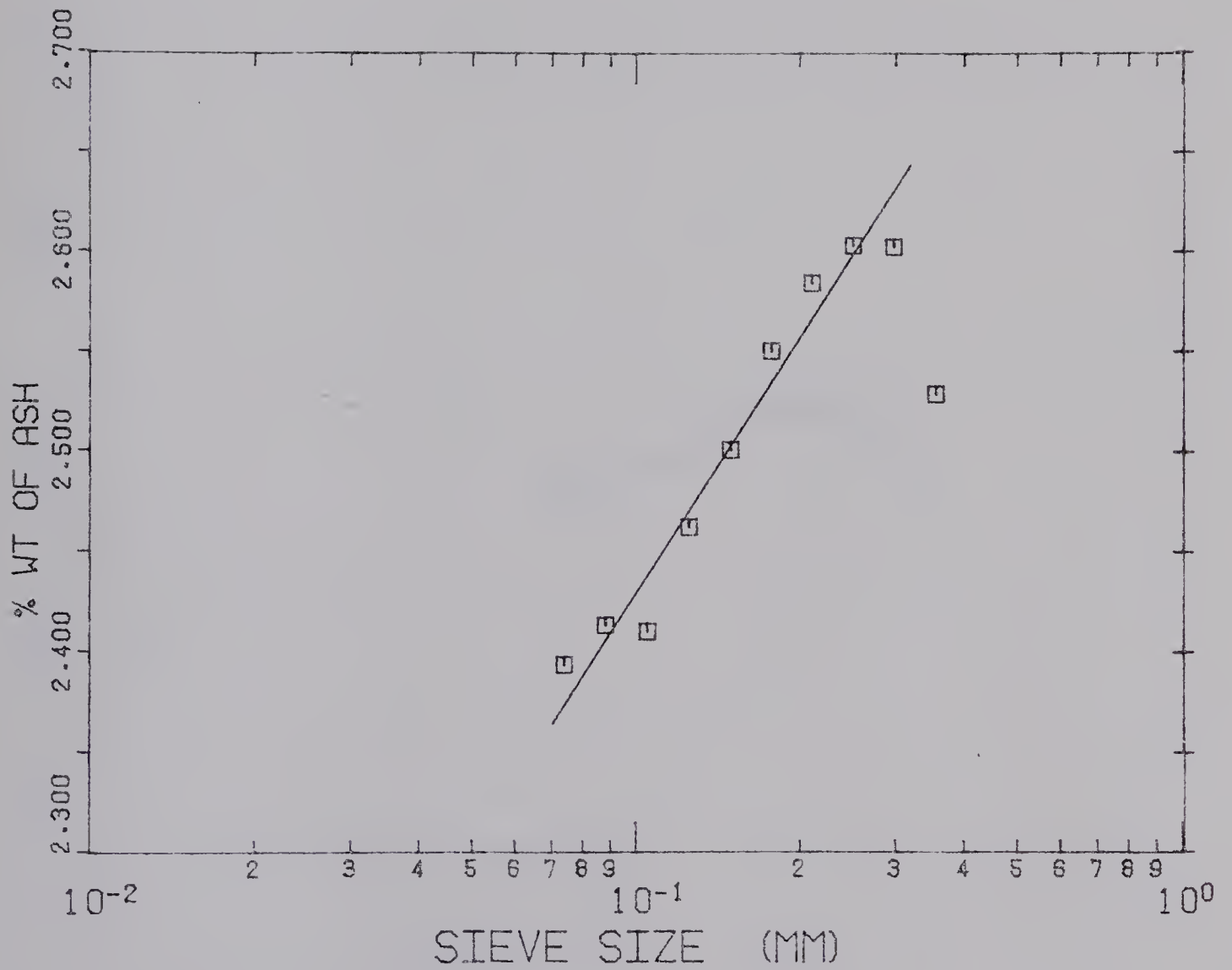


Figure 57. Vanadium Content in Fluid Coke Ash as a Function of Particle Size, Dec 7, '78.

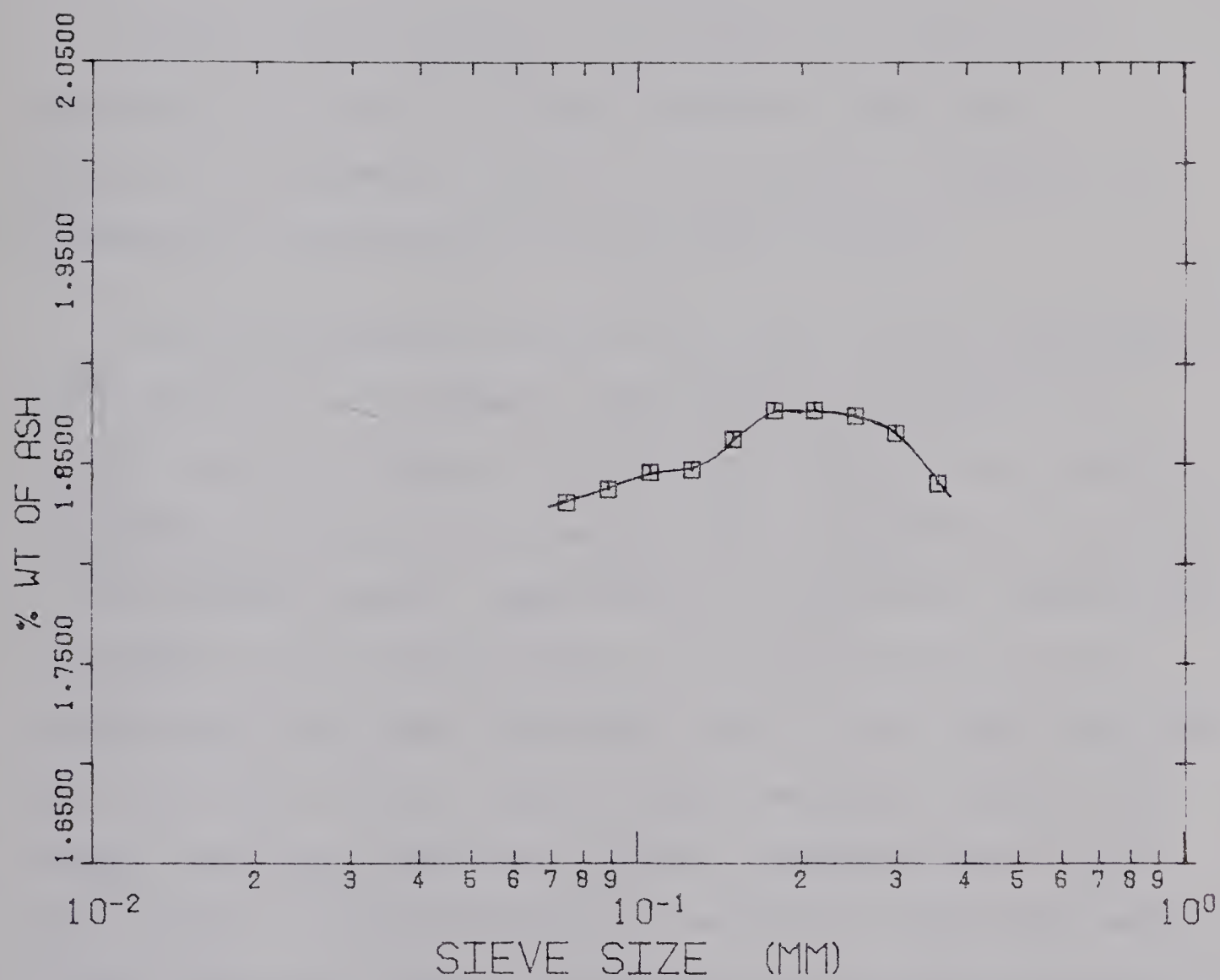


Figure 58. Vanadium Content in Fluid Coke Ash as a Function of Particle Size, Aug 12, '80.

8. Fourier Transform Infrared Spectroscopy

Some preliminary studies on the organic molecular structure of fluid coke were made by infrared spectroscopy. The spectrometer used was a Nicolet Fourier Transform Infrared Spectrometer (FT-IR) Model 7199.

Two dry samples each of 100 mesh and 42 mesh coke particles from Dec 7, '78 were ground to less than 2 microns. The prepared samples were embedded in potassium bromide and analyzed by the FT-IR spectrometer.

From the spectra (Figure 59 and 60), it was found that fluid coke is very aromatic and contains a substantial concentration of hydroxyl (-OH) functional groups. Some of the hydroxyls may be contributed from the hydrated silicates of the mineral matter. Some carbonyl functional groups were observed and they were found to be more prominent in the smaller particle size (100 mesh) than in the larger particle size (42 mesh). This is quite understandable, because the larger coke particles had a longer residence time in the fluid coker for decarboxylation. Mercapto (-SH) functional groups, which are usually indicated by peaks between 2650 to 2500 cm^{-1} , were not observed. This suggests that the organic sulphur is mainly in the form of heterocyclic ring structures. The assignment of the spectral peaks to their corresponding organic functional groups appears in Table 36.

Table 36. Absorption Bands in Infrared Spectra of Syncrude Fluid Coke

<u>Band Position (cm⁻¹)</u>	<u>Assignment</u>
3420	Hydroxyl (-OH)
3030	Aromatic (C-H)
2940	Aliphatic (C-H)
2860	Aliphatic (C-H)
1710	Carbonyl (C=O)
1690	Carbonyl (C=O)
1630	Aromatic (C=C) or H-bonded Quinoid Oxygen
1430	Aromatic (C=C)
1380	not assigned

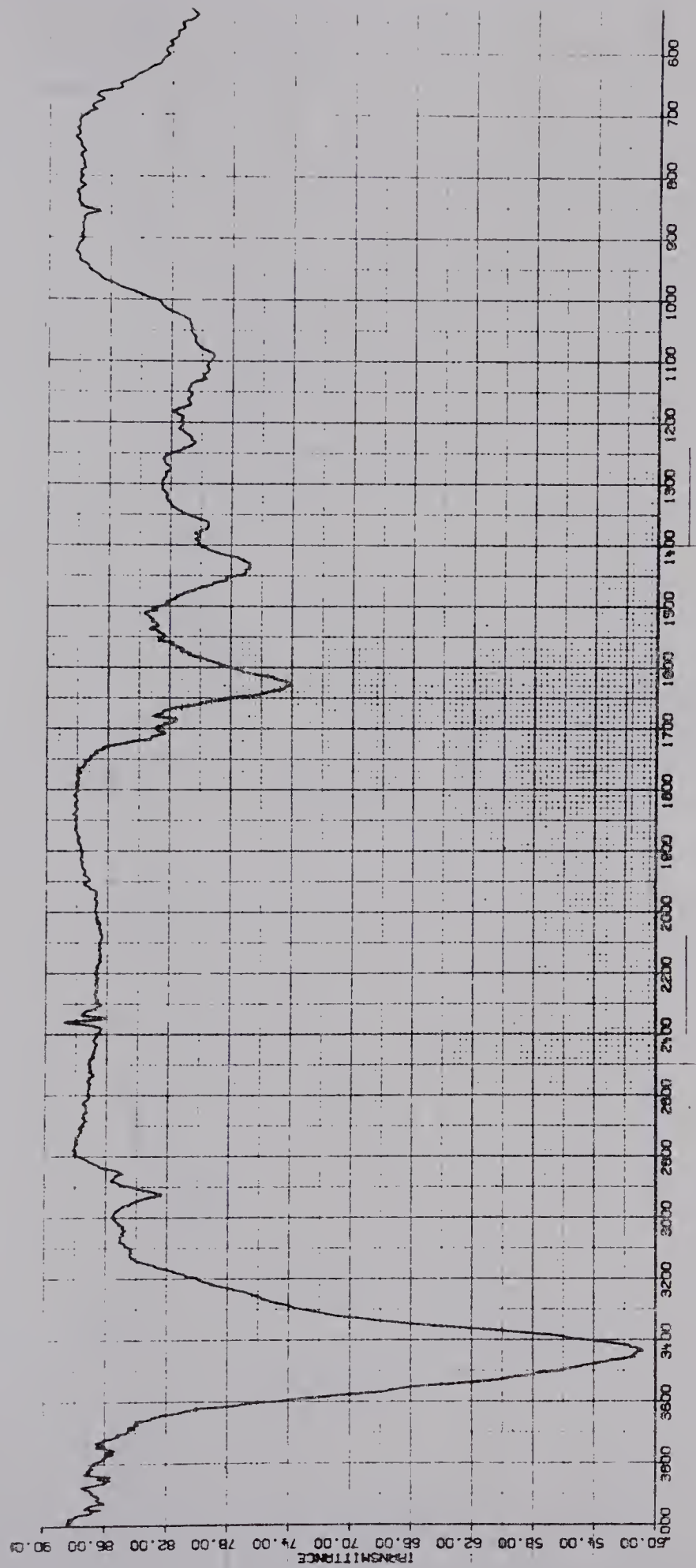


Figure 59. Fourier Transform Infrared Spectrum for 42 mesh Fluid Coke.

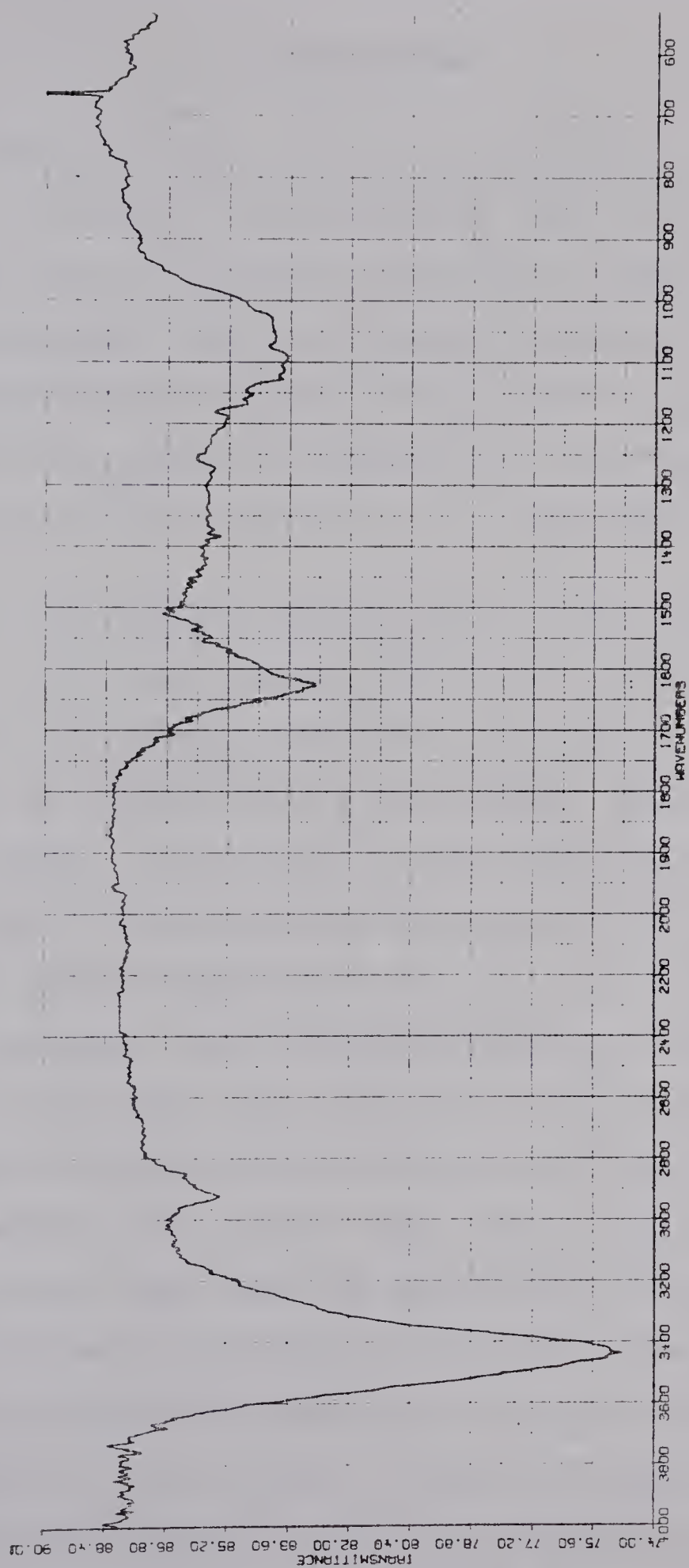


Figure 60. Fourier Transform Infrared Spectrum for 100 mesh Fluid Coke.

9. Conclusions

Syncrude fluid coke is a fairly homogeneous material compared to naturally occurring fossil fuels such as coal. Hence, the nature of Syncrude fluid coke is more predictable than that of fossil fuels. As a matter of fact, fluid coke may be considered as a synthetic material. Its nature is governed by the production parameters of the fluid coking process as well as the quality of its feed stock.

In the fluid coking process, it is very likely that fluid coke originates from the high boiling point, polyaromatic and hydrogen-deficient fractions of the feed stock which are deposited on mineral matter nuclei inside the coker. Hence, fluid coke is less complex than its feed stock, as the low boiling point fractions of the feed stock become the liquid or gaseous products of the process. During the coking process, the low boiling point and hydrogen-rich fractions of the feed stock are partially hydrogenated at the expense of dehydrogenation of high boiling point and hydrogen-deficient fractions. Thus, the hydrogen-deficient fractions of the feed stock are polymerized by dealkylation, hydrogen elimination and aromatization until they become a solid-like material. This solid-like material will very likely deposit on the surface of fluid coke particles which provide heat and surface for the coking reaction. In other words, the process may be considered as a heterogeneous nucleation process, in which fluid coke particles serve as

nuclei for the formation and growth of solid materials in the fluid coker. Hence, fluid coke is a very hydrogen-deficient material (atomic H/C = 0.25).

During the coking process, which takes place at 950° F (510° C), mercapto functional groups (S-H) are eliminated as hydrogen sulphide. Thus, most of the organic sulphur found in fluid coke is likely in a heteroaromatic form. This phenomenon was observed in the FT-IR spectra of Syncrude fluid coke. Since the organic sulphur content is higher in the high boiling point fractions, the concentration of sulphur in the fluid coke (7-8 wt %) is greater than that in the bitumen which was found to be approximately 5 wt %.

Raw bitumen, the feed stock of Syncrude fluid coke, contains some minute particles of alumino-silicate minerals. These mineral particles may serve as the sites for coke formation. Hence, they may be considered as an intrinsic catalyst for the coking reactions. As a coke particle grows in size by deposition of solid organic matter on its surface, the weight percent of mineral matter decreases. This was corroborated experimentally as it was found that smaller particles have higher ash contents (Table 13 and Figure 4). This trend is common to all batches of coke analyzed in this research. Of course, some relatively large mineral particles may be accidentally fed into the fluid coker and cause some irregularity in the trend. This phenomenon was observed in the experimental results. In

Figure 4, it is seen that the coke particles which are greater than 300 microns (42 mesh) start to reverse the trend. Nevertheless, only about 5 wt % of each batch of coke received contained particles greater than 300 microns in size. In terms of the population of coke particles, the number of particles greater than 300 microns becomes insignificant.

For the inorganic matter in Syncrude fluid coke, some elements such as vanadium and nickel are highly associated with the organic matter. They may be trapped inside the coke particles when petroleum porphyrins are carbonized and become solid material during the coking process. Some elements, such as titanium and iron, may or may not be affiliated with the organic matter in the coke. From the multi-elemental analyses, most of the other major elements are likely associated with the alumino-silicate mineral matter.

Since Syncrude fluid coke has a high sulphur and vanadium content, it cannot be used for the manufacture of graphite electrodes for the aluminum industry. Syncrude fluid coke cannot be sold as a metallurgical coke, because it is too fine and has high sulphur content. Coke desulphurization may not be feasible because heteroaromatic sulphur is very difficult to remove.

It seems that the only possible means of disposing of Syncrude fluid coke are combustion and gasification. Sulphur corrosion may cause problems to combustion systems, but these problems may be minimized by judicious system design. Syncrude fluid coke can be gasified by oxygen and/or steam to medium-Btu gas. During gasification, sulphur is released as hydrogen sulphide which can be removed by conventional technology. The medium-Btu gas can be consumed at the plant site. Hence, the consumption of natural gas at the plant can be decreased.

Syncrude fluid coke ash is rich in some valuable metals such as nickel, vanadium and titanium. If it is economically feasible, these metals should be recovered before the ash is discarded.

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Appendix

Table 37. Comparison of Tyler, U.S. and Canadian Standard Sieve Series

<u>Sieve</u> <u>Openings</u> <u>(microns)</u>	<u>Mesh No.</u>		
	<u>Tyler</u>	<u>U.S.</u>	<u>Canadian</u>
420	35	40	40
354	42	45	45
297	48	50	50
250	60	60	60
210	65	70	70
177	80	80	80
149	100	100	100
125	115	120	120
105	150	140	140
80	170	170	170
74	200	200	200

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